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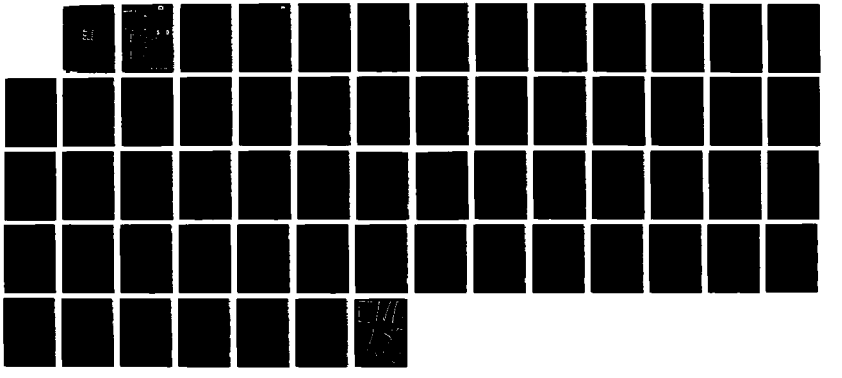

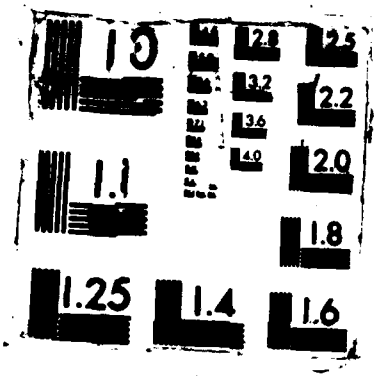
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Development of an analytical method for explosive residues in soil

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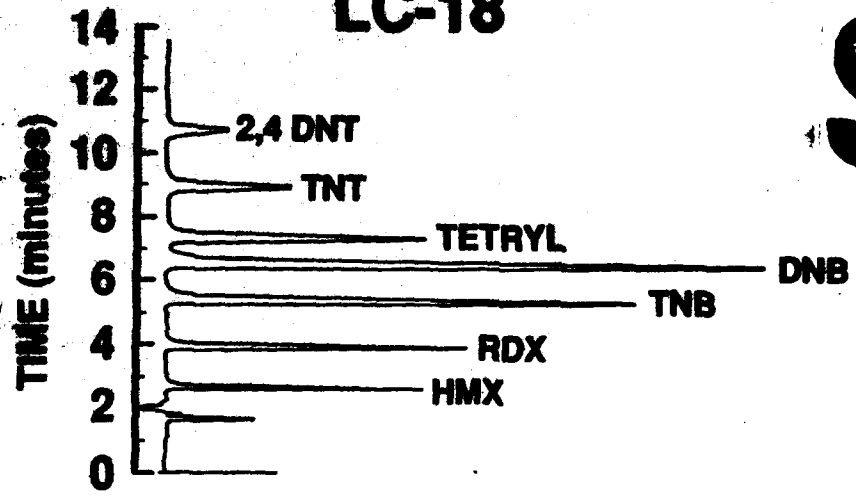

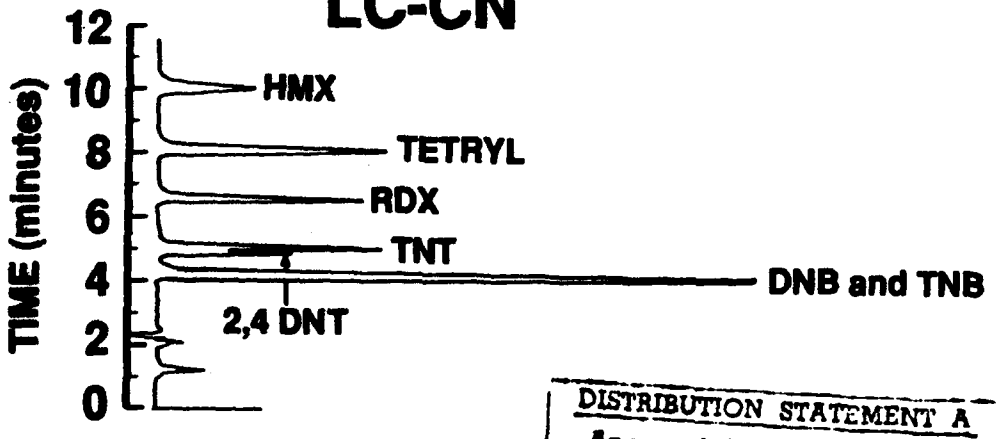

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For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

Cover: Example of the separations achieved for a standard solution on the primary and confirmation columns using the same element (1:1 water-methanol). Note the differences in elution order, particularly for HMX, RDX and TNT.

CRREL Report 87-7

June 1987

Development of an analytical method for explosive residues in soil

Thomas F. Jenkins and Marianne E. Walsh

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An analytical method was developed to determine the concentrations of HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT in soil. The method involves extracting a 2-g sample with 50 mL of acetonitrile using an ultrasonic bath procedure for 18 hr. A 10-mL portion of the extract is diluted with 10 mL of water, filtered through a 0.45-µm Millex SR filter, and analyzed by RP-HPLC using a fixed 254-nm UV detector. Separations were obtained on an LC-18 column eluted with 50:50 water-methanol. Retention times were 2.55, 3.82, 5.16, 6.25, 7.04, 8.47 and 10.15 min for HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT, respectively. Confirmation of analyte identities is recommended by RP-HPLC on an LC-CN column using 50:50 water-methanol. Kinetic studies using naturally contaminated soil indicated that equilibrium was achieved within 24 hr for the majority of soils and analytes studied.

The method provides linear calibration curves over a wide range of concentrations. Reporting limits were conservatively estimated at 1.6, 1.8, 1.5, 0.5, 5.5, 0.8 and 0.8 µg/g for HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT. Analytical precision was estimated at ± 0.44, 0.51, 0.43, 0.13, 1.24, 0.27 and 0.20 µg/g, respectively, in the range of homogeneous variance near the detection limits. At higher

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Item 19. Abstract (cont'd).

concentrations the relative standard deviation was constant at 2% for HMX, RDX, DNB and TNB, 3% for TNT and 2,4-DNT, and 6% for Tetryl. Recovery was found to be greater than 96% for all analytes from a spike-recovery study. The method was successfully tested using contaminated soil from the Iowa Army Ammunition Plant, which gave a range of analyte concentrations from near the detection limit to the percent levels.

Several types of commercial 0.45-µm filters were tested. No loss of analytes was found when 50:50 acetonitrile-water solutions were filtered.

PREFACE

This report was prepared by Thomas F. Jenkins, Research Chemist, Geochemical Sciences Branch, Research Division, and Marianne E. Walsh, Physical Scientist, Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL). Funding for this research was provided by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD (R-90 Multi-Analytical Services), Martin H. Stutz, Project Monitor.

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CONTENTS

	Page
Abstract	i
Preface	iii
Abbreviations	vi
Introduction	1
Background	1
General analytical considerations	1
Soil extraction	2
Separation and determination	3
Previous CRREL research	4
Objectives	5
Experimental methods	5
Instrumentation	5
Chemicals	6
Soils	6
Soil extraction	6
Filtration of extracts	6
Preparation of calibration standards	7
Linearity of calibration curves	8
Kinetic studies	8
Reporting limit determination	8
Accuracy	9
Precision	9
Results and discussion	9
Retention times of analytes and potential interferences	9
Instrument calibration	11
Kinetic studies	12
Spike-recovery study	14
Filtration tests	17
Summary and conclusions	19
Literature cited	19
Appendix A: Data	23
Appendix B: Chemical structures	49

ILLUSTRATIONS

Figure

1. Chromatograms of major analytes on LC-18 column eluted with 50:50 water–methanol with and without potential contaminants 9
2. Chromatograms of major analytes on LC-CN column eluted with 50:50 water–methanol with and without potential contaminants 10
3. Chromatograms of an extract from an Iowa AAP soil on LC-18 and LC-CN columns eluted with 50:50 water–methanol at 1.5 mL/min 11
4. TNT concentration vs time for the kinetic study of Iowa AAP soils 2, 3, 4 and 6 14
5. Chromatograms of soil extracts from the spike-recovery study using USA-THAMA standard soil 16
6. Reporting limit determination for DNB 17

TABLES

Table		Page
1.	Soils used in the analysis	6
2.	Types of filters tested using mixed aqueous–organic solvent containing HMX, RDX, TNT and 2,4-DNT	7
3.	Calibration standards	7
4.	Spiking solutions	8
5.	Retention times and capacity factors for primary analytes and potential interferences on LC-18 and LC-CN columns eluted with 50:50 water–methanol at 1.5 mL/min	10
6.	Concentration ranges tested during determination of detector linear range	12
7.	Regression coefficients and lack-of-fit statistics for linear calibration models	12
8.	Sensitivities for primary analytes using a 254-nm UV detector and LC-18 column	12
9.	Summary of kinetic study results for TNT, HMX, TNB, RDX, Tetryl and DNB in Iowa AAP soils	13
10.	Means and variances of found concentrations at each target level for reporting limit test	15
11.	Reporting limits, range of linearity, analytical precision and accuracy from four-day spike-recovery tests	17
12.	Summary of filtration results from HMX, RDX, TNT and 2,4-DNT in 50:38:12 water–methanonol–acetonitrile	18

ABBREVIATIONS

HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine
TNB	1,3,5-trinitrobenzene
DNB	1,3-dinitrobenzene
Tetryl	methyl-2,4,6-trinitrophenylnitramine
TNT	2,4,6-trinitrotoluene
2,4-DNT	2,4-dinitrotoluene
TAX	hexahydro-1-(N)-acetyl-3,5-dinitro-1,3,5-triazine
SEX	octahydro-1-(N)-acetyl-3,5,7-trinitro-1,3,5,7-tetrazocine
2,6-DNT	2,6-dinitrotoluene
2,4,5-TNT	2,4,5-trinitrotoluene
2-Am-DNT	2-amino-4,6-dinitrotoluene
4-Am-DNT	4-amino-2,6-dinitrotoluene
2,4-DAmNT	2,4-diamino-6-nitrotoluene
2,6-DAmNT	2,6-diamino-4-nitrotoluene
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency

Development of an Analytical Method for Explosive Residues in Soil

THOMAS F. JENKINS
MARIANNE E. WALSH

INTRODUCTION

One of the Army's major environmental problems is the presence of soil contaminated with explosive residues at many military facilities. Soil was contaminated over many years by disposal of wastewater from load-and-pack operations for munitions production, burning or detonation of off-specification material, and demilitarization of out-of-date explosives. Two of the principal components of these residues are TNT and RDX, the two high explosives used most extensively by the U.S. Army. TNT and RDX are particularly troublesome from an environmental point of view because they are relatively hydrophilic and leach readily through the soil, potentially contaminating the groundwater.

For this reason the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), under the Installation Restoration Program, has conducted soil surveys to detect and quantify explosive residues in soil at a number of military installations. These programs are usually conducted under contract, with soil analyses performed by commercial laboratories throughout the country. Generally, these laboratories are competent and use techniques that appear to be analytically sound. However, no assessment of the various analytical steps has been reported. Thus many different methods are used, undoubtedly with varying levels of performance and efficiency. This report describes the final steps of a CRREL effort to develop a standard technique for analyzing explosive residues in soil.

BACKGROUND

General analytical considerations

Analyzing organic chemical residues in soils is a three-step process: extracting the soil with an organic solvent, separating individual components, and determining identities and concentrations using detectors sensitive to the specific compounds. Depending on the nature of the analytes, the organic solvents used for extraction have ranged from hexane or methylene chloride, which are nonpolar, to acetone, methanol or acetonitrile, which are quite polar.

Some types of extraction, such as shaking or sonicating the soil in the presence of an extraction solvent, rely on a favorable distribution coefficient for the analyte between the organic solvent and the soil. The distribution coefficient is maximized when the extraction solvent is one in which the analytes are highly soluble. Sequential extractions are often used to achieve complete recovery.

The Soxhlet extractor has also been used for extracting organic residues from soil. Since extracted analyte is continuously removed from contact with soil each time the solvent siphons, the Soxhlet is particularly effective for removing analytes with low distribution coefficients.

For both types of extraction the solvent must wet the soil surface. Soils collected from the field have water contents ranging from a few percent to well over 100% on a dry weight basis. To wet the surface of these soils with an organic solvent, either the water must be removed by an initial drying step or a water-miscible solvent must be used. An initial drying step also allows soil samples to be homogenized efficiently before subsampling, something not possible with wet soils.

Determination of explosives in the extracts always requires a separation step since multiple analytes are always present. The two most popular approaches have relied on either gas chromatography (GC) using electron capture (ECD), thermal electron (TEA) or mass spectrometric (MS) detection or high-performance liquid chromatography (HPLC) generally using UV detection. When GC is used, the solvent must be preconcentrated to achieve low detection limits since only a few microliters of sample can be injected in the instrument. Since GC relies on analytes moving through a column at an elevated temperature in the gas phase, it works best for relatively volatile compounds that are not thermally la-

bile. Since RDX and HMX are known to be thermally labile, detecting them with GC is analytically difficult and unpredictable.

In HPLC, on the other hand, analytes move through the column at ambient temperature in solution. Much larger sample volumes can be used, often eliminating the need for solvent concentration prior to analysis.

Soil extraction

A variety of procedures and solvents have been studied for extracting organic substances from solid matrices. Kooke et al. (1981) compared the extraction efficiency of the Soxhlet extractor, manual shaking and the ultrasonic bath for dibenzodioxins and dibenzofurans in fly ash. The extraction solvents were toluene, methylene chloride, chloroform, benzene and 50:50 acetone–hexane. The authors concluded that Soxhlet extraction for 24 hr with either benzene or toluene achieved the highest recovery and reproducibility for both types of analytes. However, it appears that insufficient experimental replication was used to ensure that differences were statistically significant relative to experimental random error.

Peterson and Freeman (1982) compared the efficiency of Soxhlet extraction vs ultrasonic bath equilibration for extracting phthalate esters from spiked, dried sediment. The Soxhlet method used methanol for 24 hr followed by methylene chloride for 48 hr. The sonic bath method used three successive portions of methylene chloride for two minutes each. Even with much shorter times, the sonic bath method was superior.

Johnsen and Starr (1972) also compared the extraction efficiency of the Soxhlet method vs sonication. They compared the recovery of dieldrin, heptachlor and several other organochlorine pesticides from spiked dry soil using an ultrasonic probe, an ultrasonic bath and the Soxhlet extractor. Acetone was the extraction solvent, and the soil was spiked a month before extraction. The use of the sonic probe for 30 s achieved better recovery than 8 hr with the Soxhlet method. The sonic bath was as effective as the sonic probe for high clay soil using a 20-min equilibration time. For the sonic probe, acetone was superior to petroleum ether, hexane–acetone, ethanol and benzene–methanol.

Junk and Richard (1986) studied the efficiency of extraction of polycyclic organics from spiked fly ash using the sonic probe and the Soxhlet extractor and using pyridine, benzene, cyclohexane, methylene chloride, dimethyl sulfoxide, dimethyl formamide and N-methylpyrollidone as solvents. No technique or solvent was consistently superior, although they recommended the polar solvent pyridene. They further stated that "efficient recovery of a specific compound from a particular solid matrix is achieved by tailoring both the extraction technique and the solvent."

Fowlie and Bulman (1986) also compared the efficiency of the ultrasonic probe vs the Soxhlet method in recovering anthracene and benzopyrene from soil. They compared a 16- to 18-hr extraction period using the Soxhlet with a hexane–acetone solvent vs 2 min using the sonic probe in acetone. The Soxhlet procedure achieved higher average recovery (74.5% vs 62.8%), but no attempt was made to ensure that 2 min were sufficient to achieve equilibration with the probe.

Sporstol et al. (1983) achieved similar results when they compared the Soxhlet and the sonic probe. Their Soxhlet procedure used a dried sediment, methylene chloride and a 20-hr extraction period. Their sonic probe method used wet sediment with two portions of methylene chloride or methylene chloride–methanol (95:5) for 15 min each. The Soxhlet procedure achieved higher recovery, but the sonic probe with methylene chloride–methanol was clearly superior for polar analytes. Direct comparison seems unjustified, however, since the sediment was dried for the Soxhlet method but not for the sonic probe.

Another study was conducted in which the Soxhlet procedure was compared with an equilibrium batch extraction method based on shaking the soil in the presence of the extracting solvent (Wegman and Hofstee 1982). They extracted organochlorines from clay, peat and river sediment using acetone, petroleum ether and acetone–petroleum ether. Both wet and dry soils were studied. The authors concluded that recovery for the 15 organochlorine compounds studied was higher for the shaking procedure using acetone, although it is unclear whether the differences were statistically significant.

A number of other studies have compared various solvents using a single extraction method. Miller et al. (1983) compared acetone, acetonitrile, methylene chloride–methanol and hexane as solvents for extracting nitroorganics from sediments using the batch wrist-action shaking procedure. Overall, the authors recommended methylene chloride–methanol (95:5) because the polar solvents extracted additional explosive residues that caused analytical interferences, although poor recovery of Tetryl was observed. Freeman and Cheung (1981) also compared solvents for extracting diethylhexylphthalate (DEHP) from dried sediment. They used a method based on batch ultrasonic agitation and Soxhlet extraction and compared methylene chloride with various other solvents. The recovery with methylene chloride was significantly greater than with the other solvents, possibly because of greater gel swelling and equivalent solubility parameters between solvent and analyte. In addition, the authors stated, "Desorption of a solute also depends on its solubility in the extracting liquid. For convenience, we use the rule that like dissolves like and predict a solubility maximum when the solute and solvent

are matched." Solubility parameters for methylene chloride and DEHP are very similar.

Grosjean (1975) also compared extraction solvents using the Soxhlet method. He studied the recovery of organics from trapped aerosol particles using a wide range of pure and binary solvent systems. He concluded that to extract organics that varied widely in polarity, a binary organic solvent containing nonpolar and polar components was best. To extract only the polar organics, a polar solvent was best. Haddock et al. (1983) also compared various organic extractants using the Soxhlet method. The authors studied the extraction of anthracene from spiked wet and dried sediment samples after various equilibration periods. The solvents were benzene, acetonitrile–benzene and acetone–cyclohexane–methanol. Acetonitrile–benzene was generally found to be superior to benzene alone. Recovery from air-dried sediment was generally higher than for wet sediment. When anthracene was allowed to interact with wet sediment, it was significantly harder to extract, possibly due to the movement of anthracene into interclay lattices.

In a similar study, Harrold and Young (1982) studied the Soxhlet extraction of priority pollutants from model solids using various extraction solvents. Hexane, benzene, methylene chloride and hexane–methylene chloride were tested. The least polar solvent, hexane, showed the poorest performance. The other three gave similar results. The authors also determined that an extraction time of 24 hr was optimum; longer extraction times resulted in loss of the analyte.

Goerlitz and Law (1975) reported a method for extracting TNT and RDX from soil using a batch wrist-action shaker procedure. The spiked soil was sequentially extracted, first with acetone and then three times with hexane. Mean recoveries were 95% for TNT and 85% for RDX.

Smith (1976) used a sonic probe extraction method with 10% aqueous acetonitrile as the extraction solvent. Soils were fortified with a series of 13 herbicides and extracted for 2 min. Recovery percentages were found to be quite reproducible and generally ranged in the high 90s.

Cotterill (1980) also studied the extraction of herbicide residues from soil using shaking and reflux extraction methods. He used soil containing weathered herbicide residues and tested several extraction solvents, including 10% aqueous acetonitrile, methanol, 25% aqueous methanol and chloroform. Aqueous methanol was recommended. Aqueous acetonitrile was also acceptable, although it resulted in higher background levels by GC-ECD analysis.

While the available literature gives some information, it is difficult to extend the findings to extraction of explosive residues from soil. Where different extraction methods were compared, information was not usually provided to ensure that the tests were allowed to reach equilibrium. Thus low recovery for a given method might well be due to slow desorption kinetics rather than the inability of the method to achieve extraction. The work by Harrold and Young (1982), where extraction time was explicitly studied, was a notable exception.

Where methods or solvents were compared, only rarely was sufficient experimental replication used to ensure that results had statistical validity. Reported standard deviations were often greater than the differences between mean extraction efficiencies, indicating that differences would not be significant at any acceptable level of confidence.

When polar and nonpolar solvents were compared, extraction efficiencies were generally higher when a polar solvent or a mixed solvent containing a polar component was used. Polar solvents were superior even when the analytes of interest were not polar. The work on the Soxhlet extractions of DEHP (Freeman and Cheung 1981) was an exception. For more-polar analytes such as herbicide residues, a polar extracting solvent such as methanol or acetonitrile was found to be quite effective (Smith 1976, Cotterill 1980).

Most of the studies rely on fortified solids. Johnsen and Starr (1972) allowed their spiked samples to age for a month prior to extraction, but most researchers extracted immediately or soon after spiking. Analyte spiked into soil was harder to recover as the time allowed for the analyte to interact with the solid was increased (Haddock et al. 1983). Therefore, extraction results might be different if the contaminants had been allowed to interact "naturally" with the biological and chemical components of the soil as they would at a field site.

Separation and determination

Once the explosive residues are extracted into a suitable solvent, the next step is to determine the identity and concentration of individual components. Analytically this problem is similar to water analysis for these same substances, and the methods used are often extensions of water methods. Jenkins et al. (1984) reviewed applicable water methods and found that GC and HPLC methods were the most suitable for analyzing explosives in water. Since this review a number of additional papers have been published using both techniques.

Phillips et al. (1983) used a method for analyzing nitrobenzene and the isomers of dinitrobenzene in biosludges that was based on a shake-out, centrifugation technique for extraction and determination using GC/TEA (Thermal Energy Analyzer). These researchers reported an average recovery of 81% using their extraction procedure, with detection limits of about 0.05 mg/L. TEA was compared with the electron capture (ECD) and Hall electrolytic conductivity detectors and found to be

superior due to a high degree of selectivity for nitroaromatics. No information was presented, however, about the effectiveness of the method for nitramines.

Krull et al. (1983) developed a method for determining nitroorganics using GC and relative responses from ECD and photoionization detectors. Weinberg and Hsu (1983) compared GC and GC/MS techniques for analyzing nitroaromatics. Both reports include detection limits, precision and linear ranges, but neither includes results for nitramines.

Richard and Junk (1986) described a method for analyzing munitions in water that involves sample concentration on XAD-4 resin, extraction using ethyl acetate, and determination by GC on a capillary column using an ECD. Nitroaromatics and RDX were determined but no data were reported for HMX.

Another method for explosives analysis uses HPLC separation and thermospray mass-spectrometric determinations (Voyksner and Yinon 1986). This is a very powerful method for determining both nitroaromatics and nitramines. This instrumentation is limited to a very few research organizations, however, and analysis is quite expensive.

Jenkins et al. (1986) developed a direct water method for analyzing nitroaromatics and nitramines that uses reversed-phase HPLC and UV detection. Detection limits were in the low µg/L range, and interlaboratory precision was estimated at less than 10% RSD (Bauer et al. 1986).

Another water method is based on HPLC separation and reductive electrochemical detection (Maskarinec et al. 1984). This method also involves analyte concentration on a resin followed by acetone extraction, solvent exchange to ethanol, and determination using reversed-phase HPLC. The response of the electrochemical detector is compared to UV detection at 210 nm. The authors prefer the electrochemical detector because of its sensitivity for explosives and freedom from interference. The electrochemical detector, however, is sensitive to the presence of oxygen in the samples and care must be taken to eliminate it. Electrochemical detectors are seldom found in analytical laboratories, whereas UV detectors are standard on most HPLC systems.

Burrows and Brueggemann (1985) used a gradient elution HPLC method for RDX, HMX, SEX and TAX using a C-8 column and methanol–water eluent. These four components separated well in about 14 min. No results were reported for the nitroaromatics under these conditions. River water samples analyzed by HPLC revealed the presence of these four components, but GC/MS analysis on the same samples did not detect them. Brueggemann (1986) also used a gradient elution HPLC method for determination of RDX, HMX, SEX, TAX, Tetryl, 2,6-DNT and 2,4-DNT in deactivation furnace ash. Again the mobil phase was water–methanol, but separations were achieved on a C-18 column. The explosives were extracted with acetonitrile. Samples were shaken for 30 min on a wrist-action shaker, then clarified by centrifugation and filtration through a 0.45-µm filter. Detection limits were reported based on the lowest concentration that could be reproduced three times with a % RSD less than 10. The detection limit was 0.50 µg/g, for 2,4-DNT and 1.00 µg/g for the other analytes studied.

Krull et al. (1984) tested an HPLC method for TNT, RDX, Tetryl, nitroglycerine and isosorbide dinitrate. This method relies on post-column photodegradation of the explosive-forming nitrite ion, which is detected by an electrochemical detector in the oxidative mode. This method was tested for forensic analysis of postblast residues and found to have a good potential for this application.

Bongiovanni et al. (1984) described an HPLC method similar to the method presented here. While no details were given, they outlined the following method for analyzing trace amounts of HMX, RDX, Tetryl, TNT, 2,4-DNT and 2,6-DNT in soil. Samples were equilibrated to 20–30% moisture and then homogenized. The analytes were extracted with acetonitrile. Extraction was "enhanced by sonication," but no time frame was given. Samples were centrifuged and filtered through a 0.45-µm filter prior to injection. Separations were achieved isocratically on a C-18 column with a 40:60 methanol–water mobil phase. Detection limits were determined using the Hubaux and Vos method. Based on 10 g of soil extracted with 20 mL of solvent and a 25-µL injection, these detection limits ranged from 0.45 to 0.87 ppm, except for Tetryl, which had a 4.59-ppm detection limit.

Previous CRREL research

The initial CRREL research on a methodology for analyzing explosive residues in soil was conducted by Cragin et al. (1985). This study used both the wrist-action shaker and the ultrasonic bath extraction procedures, but it did not directly compare extraction techniques. Both fortified and "naturally" contaminated soils were examined. Extraction solvents included hexane, acetone, methanol, acetonitrile and tetrahydrofuran. Overall, acetone achieved the best recovery of TNT and RDX, but its high UV absorbance masked the HMX peak entirely. Methanol and acetonitrile gave good recoveries overall and were generally equivalent. Tetrahydrofuran gave inconsistent results—higher in some cases, lower in others. Recovery of TNT using hexane was poor for fortified samples.

"Naturally" contaminated soil and sediment were used to assess various drying techniques (Cragin et al. 1985). Drying the soil is necessary to allow homogenization prior to subsampling to ensure that the analyzed portions are representative of the entire sample. Highly con-

taminated lagoon sediment extracts from undried subsamples were compared with those dried by freeze drying, air drying, microwave drying, oven drying at 45°C, infrared drying and oven drying at 105°C. Mean recoveries of freeze-dried and air-dried soil were equivalent for both TNT and RDX, while recoveries were significantly lower for the other drying methods. The worst result was for oven drying at 105°C overnight, where recovery was less than 80% for both TNT and RDX compared to the undried subsamples.

A similar drying study was conducted for a soil and a sediment containing much lower levels of explosive residues. In this study, recovery of TNT, RDX and HMX was compared using methanol extracts of wet soil, freeze-dried soil, air-dried soil, soil dried at room temperature in a desiccator, soil dried in an oven at 105°C for one hour and soil dried in an oven at 105°C overnight. For TNT, mean recoveries were equivalent for both soils for all drying methods except oven drying overnight, which resulted in significantly lower recovery. For oven drying overnight, RDX recovery was also significantly lower for both soils. For air drying, recovery of RDX was lower for one soil but not the other. Low results for air drying but not for desiccator drying are unusual since drying in a desiccator at atmospheric pressure is equivalent to air drying at reduced humidity. The authors concluded that freeze drying is preferred but that air drying at room temperature is an acceptable alternative. From a practical point of view, the differences between freeze drying and room-temperature air drying for some samples are insignificant compared with the normal variability in sampling and homogenization for environmental samples.

Cragin et al. (1985) also investigated alternatives for determining individual explosives in the soil extracts, including both GC and HPLC. They had difficulty in using GC-ECD to determine TNT, apparently because of interferences by other electron-capturing components of the soil extracts. Next, normal-phase HPLC was attempted on a silica gel column with an eluent composed of 0.5% isopropanol in hexane. Injection of extracts in solvents more polar than hexane, however, resulted in poor separation. Reversed-phase HPLC was more successful. Eluents of 35:65 isopropanol–water and 60:40 methanol–water on an LC-8 column both showed excellent separations for HMX, RDX and TNT.

Jenkins et al. (1984) developed a method for directly analyzing water samples for HMX, RDX, TNT and 2,4-DNT using RP-HPLC. Separations were also achieved on an LC-8 column, but an eluent of 50:38:12 water–methanol–acetonitrile was used. They presented information on retention times, detection limits, inter- and intralaboratory precision estimates and accuracy.

Jenkins and Leggett (1985) conducted another study in which various extraction techniques and solvents were compared for determining explosive residues in soil. Several "naturally" contaminated soils collected at the Iowa Army Ammunition Plant were extracted using a Soxhlet extractor, an ultrasonic bath, a wrist-action shaker and a soil-plant homogenizer using both methanol and acetonitrile extraction solvents. Initially each method was assessed relative to the time required to achieve equilibrium or, in the case of the Soxhlet, complete extraction. These results indicated that previous studies may not have allowed sufficient time for equilbration to occur. Thus the validity of literature results comparing extraction methods is questioned. An ultrasonic bath method using acetonitrile as the extracting solvent was recommended.

Jenkins and Leggett (1985) analyzed their soil extracts using the LC-8 column and the 50:38:12 eluent recommended in the water method (Jenkins et al. 1984). This method was fine when only HMX, RDX, TNT and 2,4-DNT were being determined. Tetryl, however, elutes only several tenths of a minute ahead of TNT, making it impossible to determine either precisely in the presence of the other.

More recently Jenkins and Grant (in press) have reported an improved separation involving the use of an LC-18 RP-HPLC column using a 50:50 water–methanol eluent. Separation of HMX, RDX, TNB, TNT, DNB, Tetryl and 2,4-DNT is excellent using an isocratic method very suitable for analyzing soil extracts.

Objectives

The objectives in this study were to complete the development of a method for analyzing explosive residues in soil. This work was designed to do the following:

- Choose the best reversed-phase HPLC column–eluent combination to achieve separation of HMX, RDX, TNB, TNT, DNB, 2,4-DNT and Tetryl from each other and potential interferences using isocratic conditions;
- Select a second reversed-phase column–eluent combination for confirming analyte identities;
- Conduct additional kinetic studies using soil "naturally" contaminated at a munitions site to establish the proper extraction time for the ultrasonic bath extraction procedure;
- Establish figures of merit for the entire analytical procedure, including reporting limits for various analytes, and analytical precision and accuracy (recovery of spiked analyte from standard soil);
- Test disposable filter membranes to ensure that the filtration of extracts does not result in analyte loss.

EXPERIMENTAL METHODS

Instrumentation

HPLC determinations were conducted on a Perkin-Elmer series 3 pump with a Rheodyne 7125 sample loop injector and a Spectra-Physics SP8300 fixed 254-

nm UV detector. The peak areas were obtained using a Hewlett Packard HP3390 A integrator.

Separations were obtained on several 25-cm by 4.6-mm (5 μm) reversed-phase HPLC columns made by Supelco. These columns included LC-8, LC-18, LC-1, LC-CN, LC-DP and LC-Diol. Quantitative results were obtained using one of the following column–eluent combinations: LC-18 using 50:50 methanol–water, LC-CN using 50:50 methanol–water, or LC-8 using 50:38:12 water–methanol–acetonitrile. Samples were introduced by overfilling either a 20-μL or a 100-μL sampling loop.

Chemicals

All analytical standards for HMX, RDX, TNB, TNT, Tetryl and 2,4-DNT were prepared from Standard Analytical Reference Materials obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. Standards were dried to a constant weight in a vacuum desiccator over dry calcium chloride in the dark.

The methanol and acetonitrile used to extract the soils and to prepare the mobile phase for HPLC determinations were either Mallinckrodt ChromAR HPLC or Baker HPLC grade solvents. Water used for diluting the extracts and preparing the mobile phase was purified using a Milli-Q Type I Reagent Grade Water System (Millipore Corporation). Methanol, acetonitrile and water were combined in the proper proportions and vacuum filtered through a Whatman CF-F microfiber filter to remove particulates and to degas the mobile phase.

Soils

Soil samples used for extraction and separations testing were obtained from the Iowa Army Ammunition Plant (Middletown, Iowa) on 25 and 26 July 1983. These soils had been contaminated with explosives several years earlier. The soils were air dried to a constant weight at room temperature, ground with a mortar and pestle, and passed through a No. 30 mesh sieve. Soils were homogenized by placing them in bottles and mixing them extensively using a roller mill.

Standard soil obtained from USATHAMA was used for spike-recovery studies. Analysis indicated it was free of interferences for the analytes investigated in this study. Table 1 describes the soils used in the tests.

Soil extraction

Soil extracts were obtained as follows. A 2-g subsample of soil was placed in a 2.5-cm by 20-cm screw-cap glass test tube equipped with a Teflon-lined cap. A 50-mL aliquot of acetonitrile was added. For routine analysis the soil was dispersed using a vortex mixer (Vanlab Model K-550-G) for 1 min and placed in an ultrasonic bath (Cole-Parmer Model 8845-60) for 18 hr. For kinetic studies the soil was dispersed as described and placed in the sonic bath for six time periods ranging from 5 min to 48 hr each. After each time increment, the test tubes were centrifuged for 5 min at 1500 rpm and a 5-mL aliquot was removed for analysis. The soil was redispersed after each time period using the vortex mixer before being returned to the sonic bath.

Filtration of extracts

Acetonitrile or methanol soil extracts were processed as follows. After centrifuging as described above, a 10-mL aliquot (5 mL for the kinetic studies) of the clear supernatant was removed using a volumetric pipet and mixed with an equal volume of water in a glass scintillation vial. The vials were shaken and allowed to stand for 15 min. The plunger was removed from a 10-mL plastic B-D syringe, and the syringe was fitted to a 0.45-μm Millex SR disposable filter assembly. A 10-mL subsample of the mixed solvent was filtered by filling the chamber, replacing the plunger and forcing the solution through the filter. This portion was wasted and a second aliquot filtered. The second portion of filtrate was saved for analysis by HPLC.

Several types of membrane filters were tested using the procedure described above. The types of filters and their composition are described in Table 2.

Table 1. Soils used in the analysis.

Soil No.	*Description*	*Clay (%)*	*Organic carbon (%)*
Iowa AAP No. 1	Demolition area	67.9	<0.5
Iowa AAP No. 2	Surface of disposal lagoon	60.3	3.00
Iowa AAP No. 3	Surface of disposal lagoon	52.5	2.25
Iowa AAP No. 4	Soil near melt and pour buildings	65.3	1.25
Iowa AAP No. 5	Drainage ditch	56.6	1.37
Iowa AAP No. 6	Surface of ordnance-burning area	52.1	0.70
Iowa AAP No. 7	Control soil (uncontaminated)	48.6	2.62
USATHAMA Stand. Soil	Control soil (uncontaminated)	53.6	1.45

Table 2. Types of filters tested using mixed aqueous–organic solvent containing HMX, RDX, TNT and 2,4-DNT.

Manufacturer	*Type of membrane*	*Pore size (μm)*	*Diameter (mm)*	*Housing composition*
Millex-HV	Durapore*	0.45	25	Polyethylene
Nalgene (green)	Cellulose acetate	0.45	25	Modified acrylic
Millex-SR	PTFE	0.5	25	Polyethylene
Spartan T	Teflon	0.45	30	Polypropylene
Bio Rad Prep Disc	PTFE	0.45	32	Polypropylene
Spartan 3	Nylon 66	0.45	3	Nylon 66
Spartan 25	Nylon 66	0.45	25	Polypropylene
Nalgene (yellow)	Nylon	0.45	25	Polypropylene†
Spectra/Por	Nylon (+ charged)	0.45	25	Polypropylene†
Gelman Acro LC25	Fluoropolymer**	0.45	25	Polypropylene
Nuclepore	Polycarbonate	0.4	25	

*Polyvinylidene difluoride
†Glass reinforced
**Naturally hydrophilic

Preparation of calibration standards

Analytical stock standards of TNT, RDX, HMX, TNB, DNB, Tetryl and 2,4- DNT were prepared by carefully weighing out approximately 100 mg of each dried Standard Analytical Reference Material to the nearest 0.01 mg, transferring it to individual 100-mL volumetric flasks and diluting it to volume with acetonitrile. Flask closures were wrapped with parafilm to retard evaporation, and the flasks were stored at 4°C in the dark.

Combined analyte stock standards were prepared by pipetting 10 mL of the TNT, TNB, DNB and DNT stock standards and 20 mL of the HMX, RDX and Tetryl stock standards into a 100-mL volumetric flask. This solution contained about 100 μg/mL of TNT, TNB, DNB and DNT and about 200 μg/mL of HMX, RDX and Tetryl. The solution was stored at 4°C in the dark.

Working standards were prepared each day. For testing the linearity of calibration curves, a series of standards were prepared by pipetting the volumes given in Table 3 into individual volumetric flasks.

For each working standard, 10 mL of standard and 10 mL of water were added to a glass scintillation vial us-

Table 3. Calibration standards.

Std.	*Aliquot of combined analytic stock (mL)*	*Size of volumetric flask (mL)*	*Solution conc. (μg/L)* *TNT, TNB DNB*	*HMX, RDX Tetryl*	*Conc. in soil (μg/g)** *TNT, TNB DNB*	*HMX, RDX Tetryl*
A	10	25	40,000	80,000		
B	10	100	10,000	20,000		
	Aliquot of Std. B					
C	10	25	4,000	8,000	100	200
D	10	50	2,000	4,000	50	100
E	10	100	1,000	2,000	25	50
F	10	250	400	800	10	25
G	5	250	200	400	5	10
H	5	500	100	200	2	4
I	1	250	40	80	1	2
J	1	500	20	40	0.5	1
K	0.5	500	10	20	0.25	0.5

*Concentrations correspond to 100% extraction with 50 mL of solvent.

ing glass pipets. The vials were capped, shaken and allowed to stand 15 min prior to injection. These injection standards were half the concentrations given in Table 3; however, this extra dilution can be ignored since the samples and standards were processed identically.

Linearity of calibration curves

The linearity of the calibration curves was determined using lack-of-fit and zero-intercept tests (Jenkins et al. 1984) as described in the USATHAMA Installation Restoration Program Quality Assurance Program (USATHAMA 1985).

Kinetic studies

A series of 2-g subsamples of naturally contaminated soils from the Iowa Army Ammunition Plant were weighed out to the nearest 0.01 g in 2.5-cm by 20-cm glass screw-cap test tubes equipped with Teflon liners. Aliquots of 50 mL of acetonitrile were added to each test tube, and the soil was extracted as described in the section titled "Soil extraction." Five-milliliter aliquots were removed for analysis after 5 min, 1 hr, 4 hr, 8 hr, 24 hr and 48 hr in the sonic bath.

Determinations for HMX, RDX, TNB, DNB, Tetryl and TNT were obtained on an LC-18 column eluted with 1.5 mL/min of 50:50 methanol–water. The retention times were 2.6, 3.8, 5.2, 6.3, 7.0 and 8.5 min, respectively. The analyte identities were confirmed on an LC-CN column eluted with 1.5 mL/min of 50:50 methanol–water. The retention times on the LC-CN column were 9.9, 6.6, 4.3, 4.3, 8.1 and 5.1 min for HMX, RDX, TNB, DNB, Tetryl and TNT, respectively.

Calibration standards were prepared as previously described and analyzed on each column to obtain response factors for each analyte. Analysis of variance and Duncan's Multiple Range Test were performed to compare the means of the replicates at each time interval.

Reporting limit determination

Reporting limits were obtained using the Hubaux and Vos (1970) method described in the USATHAMA Installation Restoration Program Quality Assurance Program (USATHAMA 1985) for Class 1 certification. Subsamples of USATHAMA Standard Soil were spiked and analyzed on four separate days as described below.

The spiking standards were prepared from the same stock standard described under the section titled "Preparation of calibration standards." These standards had analyte concentrations of about 1000 mg/L.

A combined analyte spiking stock standard was prepared as follows. Aliquots of 25 mL for the TNT, TNB and DNB stock standards and 50 mL for HMX, RDX and Tetryl were added by pipet to a 250-mL volumetric flask and brought to volume with acetonitrile. The approximate concentrations of TNT, TNB and DNB were 100 µg/mL and of HMX, RDX and Tetryl were 200 µg/mL. A series of spiking standards were prepared by adding the volumes shown in Table 4 to the prescribed volumetric flasks and bringing them to volume with acetonitrile.

A series of 2-g subsamples of USATHAMA Standard Soil were weighed out to the nearest 0.01 g in 2.5-cm by 20-cm glass screw-cap test tubes. Each tube was spiked with 1 mL of one of the spiking standards described above and allowed to stand for 1 hr. Aliquots of 50 mL of acetonitrile were added and the samples extracted as described under the section titled "Soil extraction." TNT, TNB, DNB, HMX, RDX, Tetryl and 2,4-DNT were determined on an LC-18 column eluted with 1.5 mL/min of 50:50 methanol–water. Retention times were 2.6, 3.8, 5.2, 6.3, 7.0, 8.5 and 10.2 min for HMX, RDX, TNB, DNB, Tetryl, TNT and DNT. A nitrate ion standard with a retention time of 1.7 min was the unretained species used to calculate capacity factors for each analyte. The capacity factor is a measure of the

Table 4. Spiking solutions.

Aliquot of combined analyte spiking std. (mL)	*Capacity of volumetric flask (mL)*	*Solution conc. (µg/mL)*		*Soil conc. (µg/g)**	
		TNT, TNB DNB	*HMX, RDX Tetryl*	*TNT, TNB DNB*	*HMX, RDX Tetryl*
stock	no dilution	100	200	50	100
25	50	50	100	25	50
20	100	20	40	10	20
10	100	10	20	5	10
5	100	5	10	2.5	5
2	100	2	4	1	2
1	100	1	2	0.5	1
1	200	0.5	1	0.25	0.5

*Assuming 1 mL spiking solution added to 2 g soil.

time an analyte spends associated with the stationary phase relative to the time spent in the mobile phase.

Accuracy

Analytical accuracy was estimated from the slope of the least-squares regression line from the plot of found vs target concentrations over the linear range obtained from the reporting limit determination (USATHAMA 1985).

Precision

From the results of the reporting limit tests, the range of homogenous variance for each analyte was obtained using Bartlett's Test (Jenkins et al. 1984). Within these ranges, analytical precision was estimated from the pooled standard deviation. Above this range the relative standard deviation (RSD) was found to be fairly constant and precision was estimated as % RSD.

RESULTS AND DISCUSSION

Retention times of analytes and potential interferences

The initial work centered on finding an RP-HPLC column that would separate the principal analytes from each other and potential interferences. The principal analytes, from preliminary analyses of soils from Iowa, Louisiana and Milan Army Ammunition Plants, were identified as HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT. Potential interferences, known to be present in munitions wastewater or formed by decomposition, are SEX, TAX and cyclohexanone (Stidham 1979), other isomers of dinitrotoluene (Gehring and Shirk 1967, Leggett et al. 1977), the aminodinitrotoluenes and diaminonitrotoluenes (McCormick et al. 1976, Péreira et al. 1979) and nitrobenzene (Spanggord et al. 1982). A secondary objective was to find a second RP-HPLC column that would give a very different elution order for the primary analytes, to serve as a confirmation column.

Tests were conducted with the following reversed-phase columns: LC-8, LC-18, LC-1, LC-DP, LC-CN and LC-Diol. Eluents tested were various combinations of water–acetonitrile, water–methanol and ternary phases of water–methanol–acetonitrile. LC-8 using water–methanol or the ternary phase gave good separations for HMX, RDX, TNB and TNT but failed to separate TNT and Tetryl (Appendix Table A1). A mobile phase of water–acetonitrile was unable to separate HMX and RDX.

LC-18 and LC-8 gave similar orders of elution, but TNT and Tetryl were separated by over a minute (Fig. 1) using an eluent of 50:50 water–methanol with the LC-18 column. The excellent separation for the other major analytes using LC-8 was retained or improved using LC-18. Several of the potential impurities do interfere, however. For example, TAX elutes only 0.13 min after HMX; 2,4 DAm-NT and 2,6-DAmNT also elute at about the same time as HMX, and 2,4,5-TNT elutes with TNT (Table 5).

The LC-1 and LC-DP columns were also tested with various combinations of methanol–water and the ternary mixture. Neither was successful in separating TNT and Tetryl, and the overall performance was poorer than that of either LC-8 or LC-18 (Appendix Table A1).

The LC-Diol column was tested using eluents composed of methanol–water, acetonitrile–water and 100% water. The separations were very different from those on the LC-8, LC-18, LC-1 or LC-DP columns. In general,

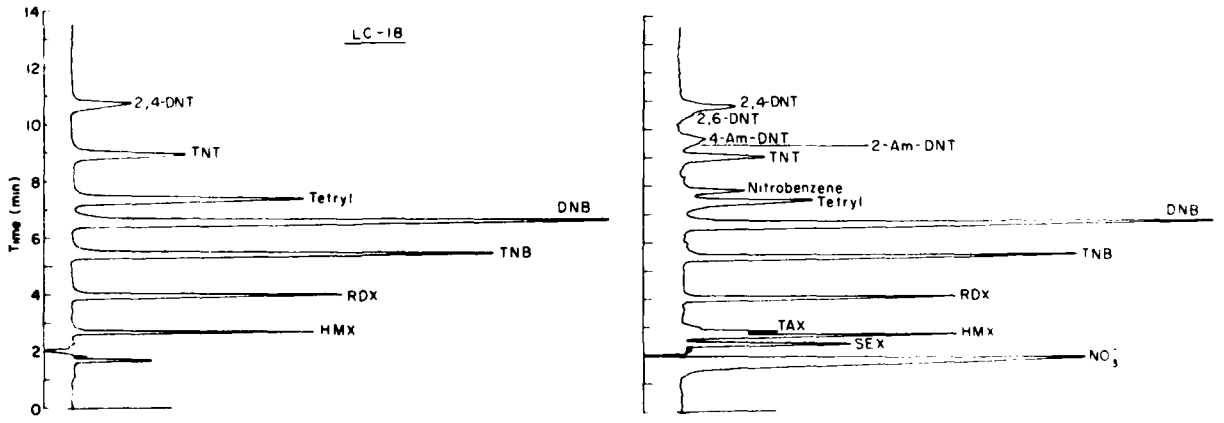


Figure 1. Chromatograms of major analytes on LC-18 column eluted with 50:50 water–methanol with and without potential contaminants.

Table 5. Retention times and capacity factors for primary analytes and potential interferences on LC-18 and LC-CN columns eluted with 50:50 water–methanol at 1.5 mL/min.

	Retention time (min)		*Capacity factor* k*	
Substance	*LC-18*	*LC-CN*	*LC-18*	*LC-CN*
HMX	2.55	9.87	0.49	3.94
RDX	3.82	6.56	1.23	2.28
TNB	5.16	4.27	2.02	1.14
DNB	6.25	4.27	2.65	1.14
Tetryl	7.04	8.08	3.12	3.04
TNT	8.47	5.11	3.95	1.56
2,4-DNT	10.15	4.94	4.94	1.47
Benzene	11.50	3.35	5.76	0.79
SEX	2.27	5.25	0.33	1.63
TAX	2.68	3.70	0.57	0.85
2-Am-DNT	9.10	5.86	4.32	1.93
4-Am-DNT	8.88	5.48	4.19	1.74
2,4-DAmNT	2.79	3.36	0.63	0.68
2,6-DAmNT	2.56	3.36	0.50	0.68
2,6-DNT	9.88	4.73	4.78	1.37
2,4,5-TNT	8.47	6.34	3.95	2.17
Toluene	23.39	--	12.8	--
Nitrobenzene	7.38	3.83	3.32	0.92
m-Nitrotoluene	14.78	--	7.64	--
Cyclohexanone	3.94	2.75	1.30	0.38

*Capacity factors are based on an unretained peak for nitrate at 1.71 min on LC-18 and 2.00 min on LC-CN.

solvent strengths had to be reduced significantly to obtain any useful separations. The best separation was with an eluent of 95% water and 5% acetonitrile. TNT was separated from Tetryl using this eluent, but for soil extracts in acetonitrile, it would be necessary to dilute the extract at least 10 to 1 with water so that the separation would not be degraded by the solvent strength of the injected sample.

The final column tested was LC-CN. This column was tested with mobile phases consisting of various combinations of methanol–water, acetonitrile–water and the ternary mixture. The best separation was using 50:50 water–methanol (Fig. 2). Separation of the primary analytes was good (with the exception of TNB and DNB), and the elution order was very different from that on the LC-18 column (Table 5). For example, HMX elutes first on the LC-8 and LC-18 columns and elutes last among the primary analytes on the LC-CN column. RDX, which elutes ahead of TNT on the other columns, elutes after TNT on LC-CN. TNT and Tetryl are very well separated on LC-CN. The LC-CN also separates TNT and 2,4,5-TNT very efficiently; the LC-18 column was unable to effect this separation. LC-CN also separates HMX from TAX and the diaminonitrotoluenes, which interfered with HMX on LC-18 (Table 5). However, as the primary analytical column, LC-CN is unsuitable because it suffers from coelution of a number of major analytes and interferences. TNT is not well separated from either of the two tested isomers of dinitrotoluene. TAX and TNB are not well separated, nor are RDX and 2,4,5-TNT (Table 5).

The final recommendation based on these tests is to use the LC-18 column as the primary analytical column for quantitative results and the LC-CN to confirm peak identities. The eluent for both columns should be 50:50 methanol–water. The elution time for all the analytes of interest on the LC-18 column using 50:50 methanol–water is approximately 75% shorter than the 40:60 methanol–water used by Bongiovanni et al. (1984), yet separations were adequate. Where two channels of HPLC equipment are available, the primary determination and confirmation can be conducted simultaneously using a common eluent. Figure 3 shows examples of

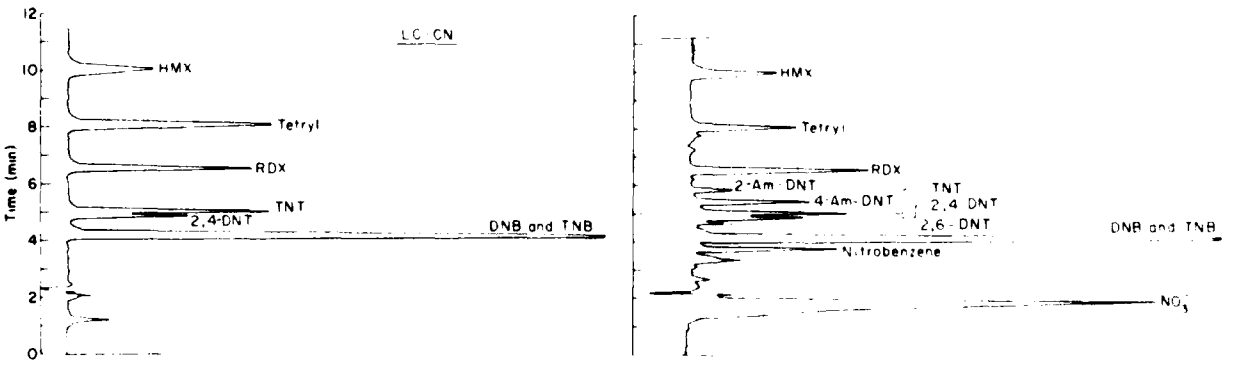


Figure 2. Chromatograms of major analytes on LC-CN column eluted with 50:50 water–methanol with and without potential contaminants.

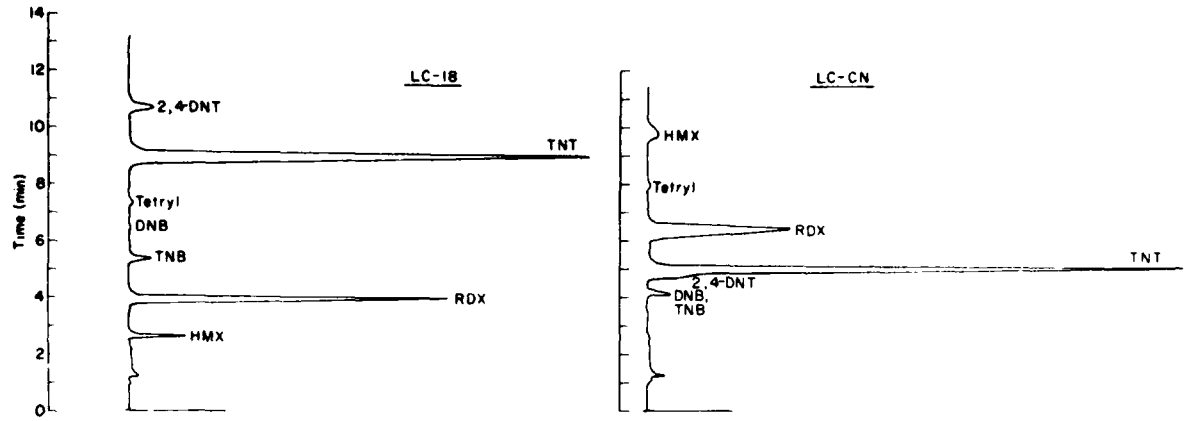


Figure 3. Chromatograms of an extract from an Iowa AAP soil on LC-18 and LC-CN columns eluted with 50:50 water–methanol at 1.5 mL/min.

chromatograms obtained using this method for an extract from an unfortified soil from the Iowa Army Ammunition Plant.

The chromatographic behavior of the aliphatic nitramines and the nitroaromatics on the LC-CN column is different from their behavior on any of the hydrocarbon-based phases. Capacity factors for HMX and RDX increase from 0.49 and 1.23 on the LC-18 column to 3.94 and 2.28 on the LC-CN column. Capacity factors for the aromatic compounds, on the other hand, decrease markedly in going from the LC-18 to the LC-CN. For example, the capacity factor for 2,4-DNT is 4.94 on the LC-18 column but only 1.47 on the LC-CN. Similar behavior is observed for TNB, DNB, the two isomers of TNT, the aminodinitrotoluenes, the diaminonitrotoluenes, nitrobenzene, 2,6-DNT and benzene. SEX and TAX, on the other hand, being acetyl deviations of HMX and RDX, behave like the aliphatic nitramines. Tetryl could be classified either as a nitramine or a nitroaromatic, and its behavior is intermediate, its capacity factor remaining about the same (3.12 vs 3.04) on the two columns.

The reason for this behavior may be a specific interaction between the -CN function on the LC-CN column and the aliphatic nitramine function of HMX, RDX, SEX or TAX. Retention on the LC-18 column appears to follow normal hydrophobic behavior, with the retention order predictable from the octanol–water partition coefficients of the analytes. A specific interaction between the -CN function and the nitramines would also explain the 20- to 30-fold increase in solubility for these compounds in acetonitrile as compared to methanol (D.C. Leggett, unpublished results).

The increase in capacity factor for the nitramines in changing from LC-18 to LC-CN is greatest for HMX and SEX, the two compounds with eight-membered rings (Appendix B). Capacity factors increase by factors of 8.0 and 5.0 for HMX and SEX compared to 1.8 and 1.5 for RDX and TAX, which have six-membered rings. When physical models of these four compounds are compared, it is clear that only in the case of the eight-membered rings can two nitramine functions interact with the same bonded -CN group. For the six-membered rings, the nitramines are too far apart for this type of interaction.

Instrument calibration

Next, a study was conducted to determine over what concentration range the detector response was linear for each of the primary analytes. Concentration ranges tested are given in Table 6. Integrator peak areas are presented in Appendix Tables A2–A8. Only those concentrations that produced peak areas are reported, except for solution blanks, which showed zero response for all seven analytes.

These data were subjected to a regression analysis using both a linear model with an intercept ($y = a + bx$) and a linear model without an intercept ($y = bx$). The coefficients obtained for a and b are presented in Table 7.

Both regression equations were then tested for lack of fit to determine if the linear models adequately described the data. For all the analytes except TNB, the F ratio for lack of fit was less than the critical value for 95% confidence, and we conclude that the linear models did adequately model the data over the concentration ranges given in Table 7 (Appendix Tables A9–A15).

A test was then conducted to determine if the intercepts obtained using the model with an intercept were significantly different from zero at the 95% confidence level (Appendix Tables A9–A15). This was done by

Table 6. Concentration ranges tested during determination of detector* linear range.

Analyte	Lowest standard tested (µg/L)	Highest standard tested (µg/L)	Range of linearity† (µg/L)
HMX	20.2	8096	202.4–4048
RDX	21.2	8480	21.2–8480
TNB	9.2	3888	19.4–3888
DNB	10.4	4176	10.4–4176
Tetryl	21.1	8448	211.2–4224
TNT	10.2	4076	20.4–2038
2,4-DNT	1.56	624	15.6–624

*254-nm UV detector, LC-18 column using 50:50 water–methanol at 1.5 mL/min, 100-µL injection volume.
†Determined using lack-of-fit statistics.

comparing the residual sum of squares for the model through the origin with the residual sum of squares of the model with an intercept (Jenkins et al. 1984). The ratios for all cases except TNB were below the critical values at the 95% confidence levels. Therefore, we conclude that linear models through the origin adequately describe the calibration data for all six of the seven analytes over the ranges listed in Table 7.

For TNB the data over the full concentration range tested was subjected to lack-of-fit tests for both models. The lack of fit was not significant for the model with an intercept, but it was barely significant for the model without an intercept. This was probably due to excellent replication, particularly at the high end of the concentration range. Plots of the data appeared quite linear, even with the zero-intercept hypothesis. Because the linear model without an intercept was accepted for the other six analytes and no major departure from linearity was observed by inspection, the linear model without an intercept was used for TNB as well.

These calibration results were also used to determine detector sensitivity values for all seven analytes. Sensitivities were calculated from peak height measurements of the highest standard considered to be in the linear range using the lack-of-fit statistics. These values, calculated in absorbance units/µg and in absorbance units/µg per L, are presented in Table 8.

Table 7. Regression coefficients and lack-of-fit statistics for linear calibration models.

Analyte	Concentration range (µg/L)	Linear model: With intercept* a	With intercept* b	Zero intercept† b
HMX	202.4–4048	2231	340.2	341.0
RDX	21.2–8480	3618	445.8	446.4
TNB	19.4–3888	-19360	932.9	925.6
DNB	10.4–4176	-594.8	1370.9	1370.6
Tetryl	211.2–4224	-23509.5	644.2	636.3
TNT	20.4–2038	9902.8	1031.6	1038.6
2,4-DNT	15.6–624	3232.5	1620.2	1627.7

* $y = a + bx$
† $y = bx$

Table 8. Sensitivities for primary analytes using a 254-nm UV detector and LC-18 column.

Analyte	Sensitivity* (Absorbance/µg)	(Absorbance/µg/L)
HMX	8.25×10^{-2}	8.25×10^{-6}
RDX	6.82×10^{-2}	6.82×10^{-6}
TNB	1.30×10^{-1}	1.30×10^{-5}
DNB	1.60×10^{-1}	1.60×10^{-5}
Tetryl	7.13×10^{-2}	7.13×10^{-6}
TNT	9.52×10^{-2}	9.52×10^{-6}
2,4-DNT	1.36×10^{-1}	1.36×10^{-5}

*Using a 100-µL loop injector, a 254-nm UV detector and an LC-18 column eluted with 50:50 methanol–water at 1.5 mL/min.

Kinetic studies

Studies on extraction kinetics were conducted on six unfortified, "naturally" contaminated soil samples from the Iowa AAP to better define the length of time required to achieve equilibrium for the ultrasonic bath extraction procedure. Concentrations of explosive residues ranged from less than the detection limit to over 15,000 µg/g. The results are presented in Appendix Tables A16–A21 and Table 9.

Table 9. Summary of kinetic study results for TNT, HMX, TNB, RDX, Tetryl and DNB in Iowa AAP soils.

	Mean concentrations (µg/g)					
Time	*Soil #1*	*Soil #2*	*Soil #3*	*Soil #4*	*Soil #5*	*Soil #6*
			TNT			
5 min	1.16(a)*	2.40(b)	14565	1285	<d(h)	849
1 hr	1.03(a)	2.77(b)	15114(e)	1410(f)	0.67(i)	872
4 hr	1.17(a)	3.96(c,d)	15141(e)	1450(g)	0.32(i)	883
8 hr	0.87(a)	3.52(b,c)	15127(e)	1405(f)	0.17(h,i)	891
24 hr	1.08(a)	4.90(d)	15377(e)	1485(g)	0.63(i)	902
48 hr	1.25(a)	4.67(c,d)	15222(e)	1470(g)	0.39(i)	928
			HMX			
5 min	<d	<d	1963	5330	<d(e)	53.0(f)
1 hr	<d	<d	2042(a,b)*	5580(c)	0.74(e)	55.5(f)
4 hr	<d	<d	2025(a,b)	5595(c)	1.13(e)	54.2(f)
8 hr	<d	<d	2016(a,b)	5580(c)	0.43(e)	56.1(f)
24 hr	<d	<d	2048(b)	5700(d)	2.45	55.0(f)
48 hr	<d	<d	2004(a)	5645(c,d)	<d(e)	59.1(f)
			TNB			
5 min	<d	<d	470	107(c)	<d	52.2(e)
1 hr	<d	<d	514(a)*	122(c,d)	<d	54.9(e)
4 hr	<d	<d	524(a,b)	126(d)	<d	52.8(e)
8 hr	<d	<d	526(b)	118(c,d)	<d	56.4(e)
24 hr	<d	<d	549	119(c,d)	<d	53.2(e)
48 hr	<d	<d	567	116(c,d)	<d	53.5(e)
			RDX			
5 min	<d	<d	13399(a)*	<d	<d	91.5(d)
1 hr	<d	<d	13793(b,c)	<d	<d	94.7(d,e)
4 hr	<d	<d	13740(b,c)	<d	<d	94.2(d.e)
8 hr	<d	<d	13709(b,c)	<d	<d	95.3(e,f)
24 hr	<d	<d	13887(c)	<d	<d	97.4(e,f)
48 hr	<d	<d	13574(a,b)	<d	<d	98.5(f)
			Tetryl			
5 min	<d	<d	279	<d	<d	<d
1 hr	<d	<d	329(a)*	<d	<d	<d
4 hr	<d	<d	324(a)	<d	<d	<d
8 hr	<d	<d	325(a)	<d	<d	<d
24 hr	<d	<d	346(a)	<d	<d	<d
48 hr	<d	<d	336(a)	<d	<d	<d
			DNB			
5 min	<d	<d	37.1	<d	<d	<d
1 hr	<d	<d	42.6(a)*	<d	<d	<d
4 hr	<d	<d	41.6(a)	<d	<d	<d
8 hr	<d	<d	43.5(a)	<d	<d	<d
24 hr	<d	<d	45.2(a)	<d	<d	<d
48 hr	<d	<d	44.5(a)	<d	<d	<d

*Values with the same letter are not significantly different at the 95% confidence level.

The concentration of TNT from soils 2, 3 and 4 reached its maximum by 24 hr. The concentration of TNT from soil 6 continued to rise through 48 hr (Fig. 4); however, the concentration of TNT increased only 3% between 24 and 48 hr.

The values for HMX showed a similar pattern, with the highest concentrations at 24 hr for soils 3, 4, and 5 and at 48 hr for soil 6. RDX levels reached a maximum by 24 hr for soil 3 and 48 hr for soil 6. A statistical analysis of the data for soil 6 indicated that the mean concentrations for HMX and RDX at 48 hr are not significantly different from the mean values at 8 or 24 hr at the 95% confidence level. Soil 6, obtained from the surface of the ordnance-burning area, may, however, have a different mode of adsorption interaction.

DNB and Tetryl were found only in soil 3, and both analytes reached maximum levels within 24 hr. For both analytes the mean concentration values for 5 min through 48 hr were not significantly different at the 95% confidence level.

The results for TNB were different for each soil where it was identified. TNB values peaked rapidly in soils 4 and 6 at 4 hr and 8 hr, respectively. In soil 6 the mean TNB concentration values for 5 min through 48 hr were not significantly different at the 95% confidence level, nor were the values from soil 4 for 1 hr through 48 hr. In contrast, TNB concentration failed to reach equilibrium by 48 hr for soil 3.

Overall, equilibrium appears to be reached by 24 hr for the majority of the soils and analytes studied. Longer extraction times may result in analyte loss, as noted for HMX and RDX. Harrold and Young (1982) also observed analyte loss during extraction periods greater than 24 hr. For the spike-recovery study, an extraction time of 18 hr was chosen for practical reasons. Samples prepared in the afternoon were thus ready for analysis the following morning.

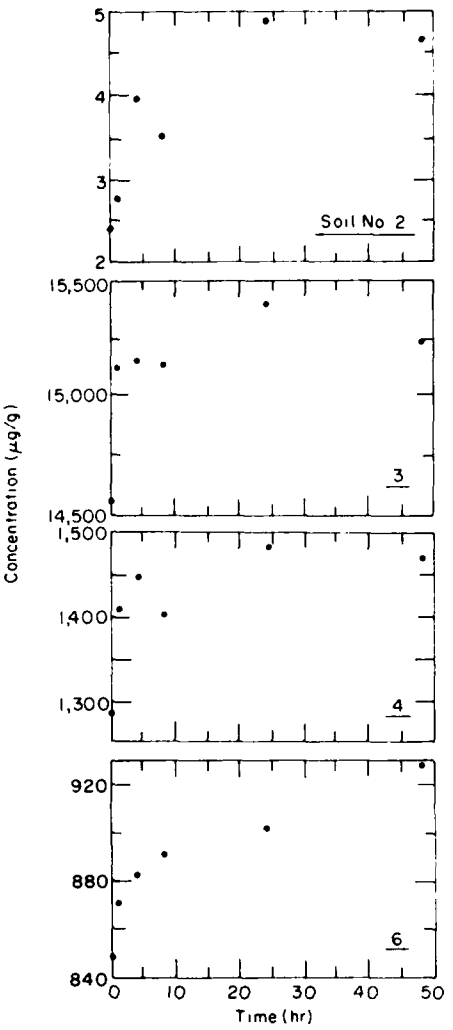


Figure 4. TNT concentration vs time for the kinetic study of Iowa AAP soils 2, 3, 4 and 6.

Spike-recovery study

A spike-recovery study was conducted to enable us to calculate the method reporting limits for each analyte as well as overall recovery and analytical precision. The study was performed as described in the U.S. Army Toxic and Hazardous Materials Agency Installation Restoration Program Quality Assurance Program (USATHAMA 1985). Estimates of reporting limits were based on the method of Hubaux and Vos (1970). Detection limits were initially estimated from signal-to-noise ratio measurements. Combined spiking solutions were prepared such that aliquots spiked onto a soil when extracted would result in analyte concentrations in acetonitrile ranging from 0.5 to 100 times the estimated detection limits. Duplicate spikes at each of the eight levels listed in Table 4 were made using USATHAMA standard soil on each of four days, and the extracts were analyzed in random order as described below. The results are presented in Appendix Tables A22–A28. Figure 5 shows three chromatograms obtained at spike levels ranging from 2x to 10x.

For reporting limit determinations the mean and variance were obtained for the observed concentrations at each target level (Table 10). Then Bartlett's test was used to determine the concentration range over which the variances were homogeneous. Homogeneous variance is a prime assumption of the Hubaux and Vos (1970) method.

Using the data in the homogeneous ranges, all eight experimentally determined concentrations were regressed against the target concentrations. Regression equations were tested for lack of fit to assess whether the assumption of a linear relationship between target and found concentrations was justified. The linear model adequate-

ly described the data in all cases at the 95% confidence level over the ranges given in Table 11.

Confidence limits about these regression lines were obtained at the 90% level. Reporting limits were obtained from the value of the target concentration X corresponding to the point on the lower confidence band where the value of the found concentration Y equals the value of Y on the upper confidence band at $X = 0$. This is shown graphically in Figure 6. Reporting limits obtained in this way are shown in Table 11. They range from 0.5 µg/g for DNB to 5.5 µg/g for Tetryl. The reporting limits for all analytes except Tetryl were less than 2 µg/g. Bongiovanni et al. (1984) also used the Hubaux and Vos method for obtaining detection limits. Detection limits of 0.45, 0.60, 4.59, 0.76, 0.58 and 0.87 for HMX, RDX, Tetryl, TNT, 2,4-DNT and 2,6-DNT, respectively, were reported. These values were based on a soil-to-solvent ratio of 1:2 and an injection volume of 25 µL. Given that the method described in this report calls for a soil-to-solvent ratio of 1:25 and an injection volume of 100 µL, the two sets of detection limits are very similar.

Analytical precision was determined by estimating the pooled standard deviation for concentrations determined to have homogeneous variances using Bartlett's test at the 95% confidence level. These values are also presented in Table 11 and range from 0.13 µg/g for DNB to 1.24 µg/g for Tetryl. Except for Tetryl, precision estimates for the analytes were at or below 0.5 µg/g for concentrations in the ranges of homogeneous variance. At higher concentrations the relative standard deviations appear to remain fairly constant at about 2% for HMX, RDX, DNB and TNB, 3% for TNT and 2,4-DNT, and 6% for Tetryl.

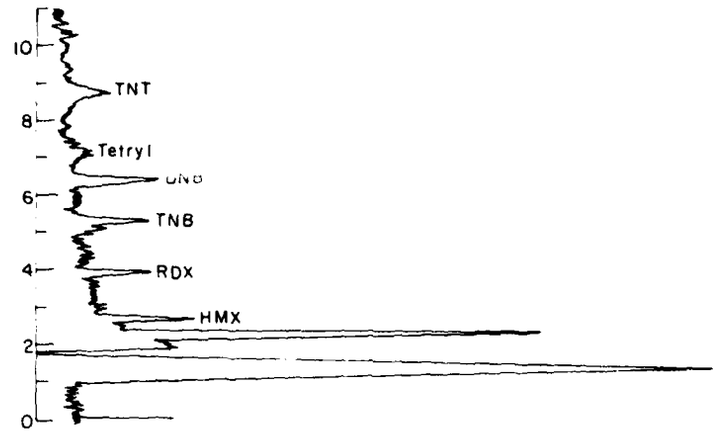
This method is clearly less analytically sound for Tetryl than for the other six analytes. This appears to be due to instability of Tetryl in acetonitrile solution. Absolute peak areas for Tetryl standards declined measurably over the course of a day. This instability appeared to lead to low recovery for low-level spikes and much poorer reproducibility for Tetryl in standards and extracts alike. Thus estimates of detection limit and precision are much poorer for Tetryl than for the other six analytes. Tetryl also had the highest detection limit for the method described by Bongiovanni et al. (1984). Bicking (1986) was unable to quantify Tetryl since it was unstable in the acetone solution in which it was stored. Within hours the Tetryl peak disappeared from sample chromatograms.

Estimates of method accuracy are presented in Table 11 and range from about 96% to 98%. Accuracy was es-

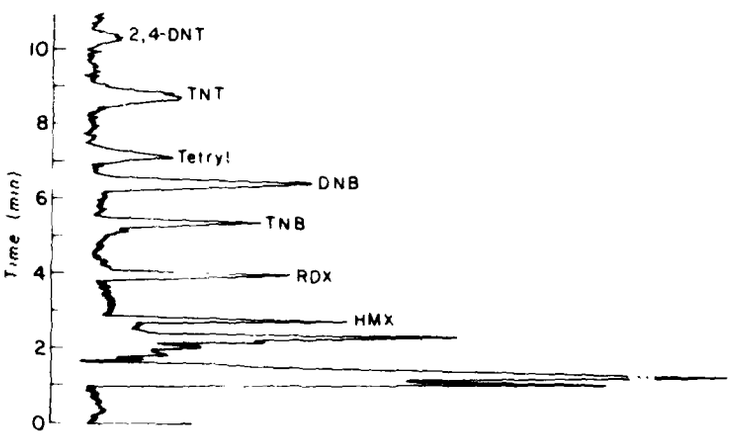
Table 10. Means and variances of found concentrations at each target level for reporting limit test.

Analyte	Target concentration (µg/g)	Found concentration (µg/g) mean	Found concentration (µg/g) variance	Bartlett's test (X^2)
HMX	0.51	0.73	0.24169	
	1.01	1.01	0.40956	
	2.02	2.51	0.13005	
	5.06	5.40	0.14905	
	10.12	10.18	0.12055	
	20.24	19.87	0.09745	5.25
	50.8	49.7	1.15513	18.56*
RDX	0.53	0.21	0.08568	
	1.06	0.86	0.16774	
	2.12	2.19	0.13357	
	5.30	5.37	0.11049	
	10.60	10.20	0.23709	
	21.20	20.35	0.27985	
	53.0	50.9	0.63588	10.09
	106.0	102.8	3.08147	41.84*
TNB	0.97	0.87	0.11611	
	2.43	2.39	0.21387	
	4.86	4.83	0.12936	
	9.72	9.56	0.33116	
	24.30	24.01	0.15046	2.60
	48.6	47.0	1.35603	17.73*
DNB	0.26	0.31	0.00847	
	0.52	0.41	0.01967	
	1.04	1.02	0.00516	
	2.61	2.55	0.02951	5.97
	5.22	4.90	0.04483	9.51*
Tetryl	2.11	1.23	0.95548	
	5.28	3.15	0.62691	
	10.56	7.05	1.84422	
	21.12	16.72	2.74090	
	52.8	49.3	5.73410	9.92
	105.6	100.4	35.50893	39.64*
TNT	0.51	0.32	0.12893	
	1.02	1.08	0.06176	
	2.55	2.94	0.02108	5.07*
	5.10	5.19	0.20023	8.22*
2,4-DNT	0.78	0.73	0.04257	
	1.56	1.70	0.01971	
	3.90	3.72	0.04588	
	7.80	7.68	0.04913	1.55

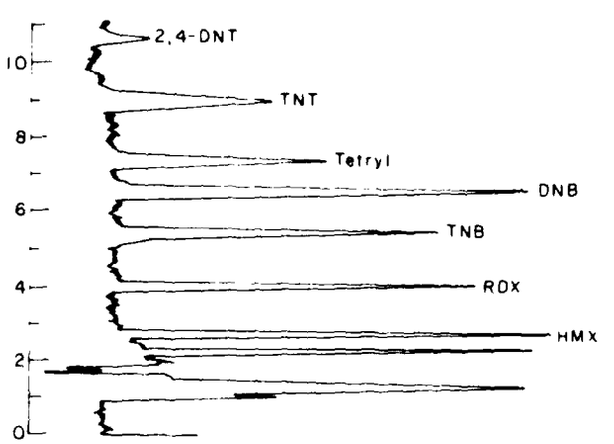
* X^2 value above critical value.



a. 2x spike level.



b. 5x spike level.



c. 10x spike level.

Figure 5. Chromatograms of soil extracts from the spike-recovery study using USATHAMA standard soil.

Table 11. Reporting limits, range of linearity, analytical precision and accuracy from four-day spike-recovery tests.

Analyte	*Reporting limit** (µg/g)	*Linear Range†* (µg/g)	*Precision†† (µg/g)*	*Accuracy*** (%)
HMX	1.6	0.51–101.2	0.44	96.4
RDX	1.8	1.06–53.0	0.51	95.9
TNB	1.5	0.97–48.6	0.43	96.9
DNB	0.5	0.26–52.2***	0.13	96.6
Tetryl	5.5	2.11–105.6	1.24	97.1
TNT	0.8	0.51–25.5	0.27	98.2
2,4-DNT	0.8	0.16–7.8	0.20	98.3

* According to method of Hubaux and Vos (1970).

† As determined by lack-of-fit statistic at the 95% confidence level.

** Slope of regression line over linear range times 100.

†† Pooled standard deviation of found concentrations over range of homogeneous variance as determined using Bartlett's test at the 95% confidence level. Homogeneous ranges for precision estimates were 0.51–20.2 µg.g, 0.53–53.0 µg/g, 0.97–24.3 µg/g, 0.26–2.61 µg/g, 2.11–21.1 µg/g, 0.51–2.55 µg/g and 0.78–7.8 µg/g for HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT, respectively.

*** Analytical precision for this analyte was so good that the lack-of-fit test detected a small departure from linearity (calculated $F = 2.4$ compared to a critical F of 1.8). From a practical standpoint, this small amount of curvature is unimportant.

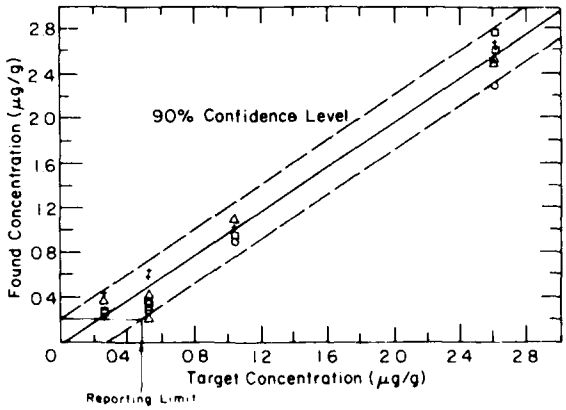


Figure 6. Reporting limit determination for DNB.

timated from the percent recovery obtained in the four-day spike-recovery study. The slope of the regression line over the linear range established using the lack-of-fit tests was multiplied by 100 to give an over-all accuracy percentage.

Filtration tests

To analyze the soil extracts by HPLC, the acetonitrile must first be diluted 50:50 with water so that the solvent strength of the sample is equivalent to that of the eluent; otherwise, peak shapes are broadened and skewed. The solution is filtered to remove fine particulates that would adversely affect the performance and longevity of expensive RP-HPLC columns. Some previous work on filtration of aqueous solutions of these explosives indicated that statistically significant losses of analyte occurred on some types of filters (Jenkins et al., in prep.).

To determine if analyte loss during filtration is also a problem for this method, a study was conducted using solutions of 50:38:12 water–methanol–acetonitrile. Analyte concentrations in unfiltered samples were compared with analyte concentrations in samples filtered through 11 different commercially available filters. The filter pore sizes were between 0.4 and 0.5 µm. Four replicates were determined for each type of filter, and the solutions were analyzed randomly. The results are presented in Appendix Tables A29–A32. Mean values and standard deviations are presented in Table 12. An analysis of variance indicates that there were no significant losses of analyte for any of the four test compounds at either of the two tested concentrations.

The 50:38:12 water–methanol–acetonitrile was tested rather than the 50:50 water–acetonitrile that would result from dilution of the soil extracts because the filtration experiment was conducted before the final extractant and eluent were selected. Tests for solubility, however, indicated that HMX and RDX are 20–30 times more soluble in acetonitrile than in methanol. Thus, if no losses were found when the 50:38:12 solution was tested, filtration of 50:50 water–acetonitrile solutions of these analytes should pose no problem.

Table 12. Summary of filtration results for HMX, RDX, TNT and 2,4-DNT in 50:38:12 water–methanol–acetonitrile.

HMX concentration (µg/L)

	Low		High	
Filter type	*Mean*	*Standard deviation*	*Mean*	*Standard deviation*
Unfiltered	237	11.2	474	6.3
Millex-HV	227	13.6	503	22.8
Nalgene (green)	240	12.2	475	14.5
Millex-SR	240	11.2	487	13.0
Spartan-T	234	7.7	469	30.2
Bio Rad Prep Disc	230	10.0	475	7.9
Spartan 3	243	9.8	477	7.5
Spartan 25	236	12.9	492	32.8
Nalgene (yellow)	239	8.8	474	5.8
Spectra/Por	249	18.2	492	19.6
Gelman Acro LC25	239	9.1	482	17.6
Nuclepore	232	5.0	505	25.0
F Ratio*	1.09		1.53	

RDX concentration (µg/L)

	Low		High	
Filter type	*Mean*	*Standard deviation*	*Mean*	*Standard deviation*
Unfiltered	205	4.6	410	11.3
Millex-HV	207	6.3	408	4.8
Nalgene (green)	212	3.3	406	7.9
Millex-SR	204	2.2	400	14.2
Spartan-T	203	4.0	392	8.8
Bio Rad Prep Disc	210	4.4	394	4.0
Spartan 3	212	6.6	403	12.6
Spartan 25	203	4.0	398	8.7
Nalgene (yellow)	206	10.2	397	10.6
Spectra/Por	207	8.1	408	13.3
Gelman Acro LC25	209	7.2	396	13.2
Nuclepore	205	3.9	392	6.2
F Ratio*	1.18		1.62	

TNT concentration (µg/L)

	Low		High	
Filter type	*Mean*	*Standard deviation*	*Mean*	*Standard deviation*
Unfiltered	107	6.3	208	9.0
Millex-HV	107	3.7	201	2.6
Nalgene (green)	107	11.1	209	2.2
Millex-SR	105	5.0	211	11.7
Spartan-T	113	6.1	196	3.6
Bio Rad Prep Disc	114	2.3	208	7.6
Spartan 3	109	4.2	204	6.1
Spartan 25	102	6.0	206	4.4
Nalgene (yellow)	107	6.6	199	5.4
Spectra/Por	107	4.9	204	9.0
Gelman Acro LC25	106	5.2	205	5.4
Nuclepore	106	4.6	208	5.9
F Ratio*	1.23		1.71	

*F Ratio at 95% confidence level from ANOVA = 2.074

2,4-DNT concentration (µg/L)

	Low		High	
Filter type	*Mean*	*Standard deviation*	*Mean*	*Standard deviation*
Unfiltered	78	3.5	159	8.8
Millex-HV	79	4.6	157	3.5
Nalgene (green)	80	4.8	159	5.6
Millex-SR	79	0.7	157	7.0
Spartan-T	82	7.3	158	8.7
Bio Rad Prep Disc	79	3.2	158	3.9
Spartan 3	81	5.6	158	2.9
Spartan 25	75	5.4	156	5.9
Nalgene (yellow)	75	3.7	160	6.2
Spectra/Por	77	1.2	161	3.9
Gelman Acro LC25	76	3.2	162	6.7
Nuclepore	81	4.3	154	5.0
F Ratio*	1.31		0.57	

*F Ratio at 95% confidence level from ANOVA = 2.074

SUMMARY AND CONCLUSIONS

A method was developed for determining HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT residuals in soil. The method involves extracting these compounds with acetonitrile using on ultrasonic bath for 18 hr. The extract is centrifuged, diluted 50:50 with water and filtered through a 0.45-μm filter. A portion of the extract is analyzed on an LC-18 reversed-phase HPLC column eluted with 50:50 methanol–water. The seven analytes elute individually over a period of 10 min. Each analyte is individually quantified on a 254- nm UV detector. Peak areas were linear with concentration, and a linear model without an intercept adequately describes the concentration-response relationship.

Reporting limits for HMX, RDX, TNB, DNB, Tetryl, TNT and 2,4-DNT were conservatively estimated at 1.6, 1.8, 1.5, 0.5, 5.5, 0.8 and 0.8 μg/g, respectively. Analytical precision ranged from 0.13 to 1.24 μg/g, and accuracy was better than 95% in all cases. Confirmation of analyte identity is recommended on an LC-CN reversed-phase HPLC column eluted with 50:50 methanol–water. The method was tested with field-contaminated soil and found to perform adequately.

The following specific conclusions were obtained:

- Separation was excellent for the seven primary analytes on an LC-18 reversed-phase HPLC column eluted with 50:50 water–methanol. A very different elution order was obtained on LC-CN using the same eluent. A combination of these two columns for quantification and confirmation of analyte identity is recommended. Separations achieved on LC-1, LC-DP, LC-8 and LC-Diol were much less desirable for these analytes.
- The response of a 254-nm UV detector was found to be linear with respect to concentration for all seven analytes. A linear model without an intercept was found to adequately describe the calibration data, allowing a one-point calibration procedure to be used.
- Six contaminated soils from the Iowa AAP were studied to determine the amount of time required to achieve equilibrium using the ultrasonic bath method of extraction. Equilibrium was reached within 24 hr for the majority of soils and analytes studied.
- A four-day spike-recovery test was conducted to allow estimation of detection limits, accuracy and precision. Except for Tetryl, detection limits and analytical precision for the analytes were better than 1.8 μg/g and 0.51 μg/g, respectively. Performance was poorer for Tetryl, apparently due to its instability in acetonitrile. Recovery for all seven analytes was greater than 95%.
- Tests of various 0.45-μm disposable filters indicated that no significant losses of analyte should occur with a solution of 50% aqueous and 50% organic solvent.

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APPENDIX A. DATA

Table A1. Retention times and capacity factors for primary analytes and potential interferences on LC-8 eluted with 50:38:12 water-methanol acetonitrile, LC-DP and LC-1 eluted with 60:40 water-methanol at 1.5 µL/min.

	Retention time (min)			Capacity factor*		
Substance	LC-8	LC-DP	LC-1	LC-8	LC-DP	LC-1
HMX	3.20	4.05	3.20	0.808	1.34	0.78
RDX	4.17	4.70	4.05	1.36	1.72	1.25
TNB	4.93	5.87	4.26	1.79	2.39	1.37
DNB	5.70	6.78	4.96	2.22	2.92	1.76
Tetryl	7.23	10.88	5.87	3.08	5.29	2.26
TNT	7.56	9.44	5.85	3.27	4.46	2.25
2,4-DNT	8.36	10.03	6.93	3.72	4.80	2.85
Benzene	--	7.04	5.13	--	3.07	1.85
SEX	2.62	3.45	2.91	0.480	0.99	0.62
TAX	2.92	3.91	2.91	0.650	1.26	0.62
2-Am-DNT	8.06	8.72	7.06	3.55	4.04	2.92
4-Am-DNT	8.23	10.88	7.06	3.65	5.29	2.92
2,4-DAmNT	2.91	4.77	3.96	0.644	1.76	1.20
2,6-DAmNT	2.69	3.81	3.47	0.520	1.20	0.93
2,6-DNT	8.77	12.40	6.75	3.95	6.17	2.75
2,4,5-TNT	8.43	12.70	7.06	3.76	6.34	2.92
Nitrobenzene	6.27	7.27	5.57	2.54	3.20	2.09
Cyclohexanone	3.76	4.86	6.10	1.12	1.81	2.39

*Capacity factors based on an unretained peak for nitrate at 1.77 min for LC-8, 1.73 min for LC-DP, and 1.80 for LC-1.

Table A2. Instrument calibration results for HMX.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
202.4	5.06	68408	74373
404.8	10.12	135740	139010
809.6	20.24	280100	274720
2024	50.60	694980	695270
4048	101.2	1377900	1376800
8096	202.4	2747100	2722900

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A3. Instrument calibration results for RDX.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
21.2	0.53	0	10884
42.4	1.06	17786	12699
84.8	2.12	54238	43156
212	5.30	107830	101010
424	10.60	188250	191910
848	21.20	391600	363520
2120	53.00	965320	950090
4240	106.0	1894500	1896700
8480	212.0	3788300	3774200

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A4. Instrument calibration results for TNB.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
19.4	0.48	5055	15238
38.9	0.97	28322	23080
97.2	2.43	77372	71908
194.4	4.86	178900	152630
388.8	9.72	350280	334870
972	24.3	872490	861550
1944	48.6	1776900	1767800
3888	97.2	3646100	3600500

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A5. Instrument calibration results for DNB.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
10.4	0.26	16241	18802
20.9	0.52	24368	30398
41.8	1.04	66488	54108
104.4	2.61	136160	144070
208.8	5.22	290620	270490
417.6	10.44	562890	583330
1044	26.10	1430000	1431900
2088	52.20	2855000	2864700
4176	104.4	5757300	5692900

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A6. Instrument calibration results for Tetryl.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
211.2	5.28	130590	111640
422.4	10.56	267410	265800
844.8	21.12	504900	530590
2112	52.80	1321100	1265300
4224	105.60	2758500	2677500

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A7. Instrument calibration results for TNT.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
20.4	0.51	15912	15938
40.8	1.02	51943	52094
101.9	2.55	98478	116680
203.8	5.10	202850	233580
407.6	10.20	462230	433740
1019	25.47	1089200	1071200
2038	50.95	2083700	2116100

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A8. Instrument calibration results for 2,4-DNT.

Concentration		Peak Area	
Solution (µg/L)	Soil* (µg/g)	Replicate 1	Replicate 2
0	0	0	0
15.6	0.39	18755	22328
31.2	0.78	61461	45119
62.4	1.56	97645	110030
156	3.90	269500	270800
312	7.80	512060	497591
624	15.60	1015500	1010300

*Calculated relative to a 2-g soil sample extracted with 50 mL of acetonitrile.

Table A9. Lack-of-fit and zero-intercept tests for HMX.

Compound: HMX
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE HMX5PKAR.DAT****

MODEL WITH INTERCEPT: Y = 2231.15 + 340.174 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	9.646899E+07	8	1.205862E+07
TOTAL ERROR	3.825631E+07	5	7651263
LACK OF FIT	5.821268E+07	3	1.940423E+07

LACK OF FIT F-RATIO EQUALS 2.536082
Critical 95% F value at (3 , 5) = 5.41 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 340.9568 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	1.205862E+08	9	1.339847E+07
TOTAL ERROR	3.825631E+07	5	7651263
LACK OF FIT	8.232993E+07	4	2.058248E+07

LACK OF FIT F-RATIO EQUALS 2.690077
Critical 95% F value at (4 , 5) = 5.19 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: 2
Critical 95% F value at (1, 8) = 5.32 .
Accept zero intercept.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
202.4	68408	74373
404.8	135740	139010
809.6	280100	274720
2024	694980	695270
4048	1377900	1376800

Table A10. Lack-of-fit and zero-intercept tests for RDX.

Compound: RDX
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE RDXPKAR.DAT****

MODEL WITH INTERCEPT: Y = 3617.722 + 445.8025 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	1.417675E+09	16	8.860468E+07
TOTAL ERROR	7.755735E+08	9	8.617482E+07
LACK OF FIT	6.421013E+08	7	9.172876E+07

LACK OF FIT F-RATIO EQUALS 1.06445
Critical 95% F value at (7 , 9) = 3.29 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 446.4276 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	1.577058E+09	17	9.276814E+07
TOTAL ERROR	7.755735E+08	9	8.617482E+07
LACK OF FIT	8.014849E+08	8	1.001856E+08

LACK OF FIT F-RATIO EQUALS 1.162586
Critical 95% F value at (8 , 9) = 3.23 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: 1.798817
Critical 95% F value at (1, 16) = 4.49 .
Accept zero intercept.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
21.2	0	10884
42.4	17786	12699
84.8	54238	43156
212	107830	101010
424	188250	191910
848	391600	363520
2120	965320	950090
4240	1894500	1896700
8480	3788300	3774200

Table A11. Lack-of-fit and zero-intercept tests for TNB.

Compound: TNB
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE TNBPKAR.DAT****

MODEL WITH INTERCEPT: Y =-19360.44 + 932.873 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	4.420797E+09	14	3.157712E+08
TOTAL ERROR	1.685231E+09	8	2.106539E+08
LACK OF FIT	2.735566E+09	6	4.559276E+08

LACK OF FIT F-RATIO EQUALS 2.164345
Critical 95% F value at (6 , 8) = 3.58 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 925.5863 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	8.292139E+09	15	5.528093E+08
TOTAL ERROR	1.685231E+09	8	2.106539E+08
LACK OF FIT	6.606909E+09	7	9.438441E+08

LACK OF FIT F-RATIO EQUALS 4.480545
Critical 95% F value at (7 , 8) = 3.5 .
LOF significant.
MODELS NOT LINEAR. DO NOT TEST ZERO INTERCEPT HYPOTHESIS.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
19.4	5055	15238
38.9	28322	23080
97.2	77372	71908
194.4	178900	152630
388.8	350280	334870
972	872490	861550
1944	1776900	1767800
3888	3646100	3600500

Table A12. Lack-of-fit and zero-intercept tests for DNB.

Compound: DNB
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE DNBPKAR.DAT****

MODEL WITH INTERCEPT: Y =-594.7778 + 1370.855 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	2.810184E+09	16	1.756365E+08
TOTAL ERROR	2.663411E+09	9	2.959346E+08
LACK OF FIT	1.467725E+08	7	2.09675E+07

LACK OF FIT F-RATIO EQUALS 7.085179E-02
Critical 95% F value at (7 , 9) = 3.29 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 1370.646 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	2.810184E+09	17	1.653049E+08
TOTAL ERROR	2.663411E+09	9	2.959346E+08
LACK OF FIT	1.467725E+08	8	1.834656E+07

LACK OF FIT F-RATIO EQUALS 6.199532E-02
Critical 95% F value at (8 , 9) = 3.23 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: 0
Critical 95% F value at (1, 16) = 4.49 .
Accept zero intercept.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
10.4	16241	18802
20.9	24368	30398
41.8	66488	54108
104.4	136160	144070
208.8	290620	270490
417.6	562890	583330
1044	1430000	1431900
2088	2855000	2864700
4176	5757300	5692900

Table A13. Lack-of-fit and zero-intercept tests for Tetryl.

Compound: Tetryl
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE TET2PKAR.DAT****

MODEL WITH INTERCEPT: Y =-23509.5 + 644.2226 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	1.083808E+10	8	1.35476E+09
TOTAL ERROR	5.348156E+09	5	1.069631E+09
LACK OF FIT	5.489926E+09	3	1.829975E+09

LACK OF FIT F-RATIO EQUALS 1.710847
Critical 95% F value at (3 , 5) = 5.41 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 636.3173 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	1.345952E+10	9	1.495502E+09
TOTAL ERROR	5.348156E+09	5	1.069631E+09
LACK OF FIT	8.111366E+09	4	2.027842E+09

LACK OF FIT F-RATIO EQUALS 1.895833
Critical 95% F value at (4 , 5) = 5.19 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: 1.934985

Critical 95% F value at (1, 8) = 5.32 .
Accept zero intercept.

%%

TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
211.2	130590	111640
422.4	267410	265800
844.8	504900	530590
2112	1321100	1265300
4224	2758500	2677500

Table A14. Lack-of-fit and zero-intercept tests for TNT.

Compound: TNT
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE TNT3PA.DAT****

MODEL WITH INTERCEPT: Y = 9902.75 + 1031.581 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	3.960996E+09	12	3.30083E+08
TOTAL ERROR	1.730555E+09	7	2.472221E+08
LACK OF FIT	2.230441E+09	5	4.460882E+08

LACK OF FIT F-RATIO EQUALS 1.804403
Critical 95% F value at (5 , 7) = 3.97 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 1038.592 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	4.799333E+09	13	3.691794E+08
TOTAL ERROR	1.730555E+09	7	2.472221E+08
LACK OF FIT	3.068778E+09	6	5.114629E+08

LACK OF FIT F-RATIO EQUALS 2.06884
Critical 95% F value at (6 , 7) = 3.87 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: 2.539775
Critical 95% F value at (1, 12) = 4.75 .
Accept zero intercept.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
20.4	15912	15938
40.8	51943	52094
101.9	98478	116680
203.8	202850	233580
407.6	462230	433740
1019	1089200	1071200
2038	2083700	2116100

Table A15. Lack-of-fit and zero-intercept tests for DNT.

Compound: DNT
Units of Measure: ug/L
Response as: Peak Areas
Analysis Performed on: 6/9/86

****ANALYSIS OF RESIDUAL VARIATIONS FOR DATA IN FILE DNTPKAR.DAT****

MODEL WITH INTERCEPT: Y = 3232.5 + 1620.171 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	8.994161E+08	10	8.994161E+07
TOTAL ERROR	3.356488E+08	6	5.594146E+07
LACK OF FIT	5.637673E+08	4	1.409418E+08

LACK OF FIT F-RATIO EQUALS 2.519452
Critical 95% F value at (4 , 6) = 4.53 .
LOF insignificant.

MODEL WITHOUT INTERCEPT: Y = 1627.694 X

SOURCE OF VAR.	SUM OF SQUARES (SS)	DEG. OF FREEDOM (df)	MEAN SQUARE (MS)
RESIDUAL	9.662628E+08	11	8.784208E+07
TOTAL ERROR	3.356488E+08	6	5.594146E+07
LACK OF FIT	6.30614E+08	5	1.261228E+08

LACK OF FIT F-RATIO EQUALS 2.25455
Critical 95% F value at (5 , 6) = 4.39 .
LOF insignificant.

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ZERO INTERCEPT HYPOTHESIS

Calculated F: .7432236
Critical 95% F value at (1, 10) = 4.96 .
Accept zero intercept.

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TABLE OF DATA POINTS

CONC. (ug/L)	INSTRUMENT	RESPONSE
15.6	18755	22328
31.2	61461	45119
62.4	97645	110030
156	269500	270800
312	512060	497591
624	1015500	1010300

Table A16. Kinetic study results for TNT.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 min	1.20	2.11	14446	1270	0.00	850
	1.11	2.68	14684	1300	0.00	848
1 hr	1.17	3.09	15110	1400	0.41	875
	0.88	2.45	15118	1420	0.94	868
4 hr	1.04	3.96	15127	1440	0.00	884
	1.30	3.95	15155	1460	0.63	882
8 hr	1.13	3.24	15131	1420	0.34	890
	0.60	3.79	15123	1390	0.00	892
24 hr	1.09	5.64	15430	1480	0.73	899
	1.07	4.16	15323	1490	0.53	904
48 hr	1.12	4.43	15429	1480	0.54	925
	1.37	4.91	15014	1460	0.23	931

Table A17. Kinetic study results for HMX.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 min	0.00	0.00	1951	5290	0.00	52.5
	0.00	0.00	1974	5370	0.00	53.4
1 hr	0.00	0.00	2037	5580	0.00	54.2
	0.00	0.00	2046	5580	1.49	56.8
4 hr	0.00	0.00	2022	5540	1.07	54.9
	0.00	0.00	2027	5650	1.18	53.4
8 hr	0.00	0.00	2015	5560	0.00	52.2
	0.00	0.00	2016	5600	0.86	60.0
24 hr	0.00	0.00	2053	5670	2.62	53.1
	0.00	0.00	2043	5730	2.28	56.8
48 hr	0.00	0.00	2033	5630	0.00	60.5
	0.00	0.00	1974	5660	0.00	57.7

Table A18. Kinetic study results for TNB.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 mins	0.00	0.00	467	104	0.00	51.9
	0.00	0.00	472	109	0.00	52.4
1 hr	0.00	0.00	513	112	0.00	53.7
	0.00	0.00	514	131	0.00	56.1
4 hrs	0.00	0.00	524	121	0.00	49.5
	0.00	0.00	524	131	0.00	56.1
8 hrs	0.00	0.00	525	118	0.00	54.5
	0.00	0.00	526	118	0.00	58.3
24 hrs	0.00	0.00	549	118	0.00	50.0
	0.00	0.00	549	120	0.00	56.3
48 hrs	0.00	0.00	575	107	0.00	52.5
	0.00	0.00	558	124	0.00	54.5

Table A19. Kinetic study results for RDX.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 mins	0.00	0.00	13287	0.00	0.00	90.4
	0.00	0.00	13510	0.00	0.00	92.5
1 hr	0.00	0.00	13798	0.00	0.00	93.6
	0.00	0.00	13788	0.00	0.00	95.7
4 hrs	0.00	0.00	13727	0.00	0.00	93.1
	0.00	0.00	13753	0.00	0.00	95.2
8 hrs	0.00	0.00	13699	0.00	0.00	94.5
	0.00	0.00	13719	0.00	0.00	96.0
24 hrs	0.00	0.00	13907	0.00	0.00	95.6
	0.00	0.00	13866	0.00	0.00	99.1
48 hrs	0.00	0.00	13768	0.00	0.00	97.8
	0.00	0.00	13380	0.00	0.00	99.1

Table A20. Kinetic study results for DNB.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 mins	0.00	0.00	37.4	0.00	0.00	0.00
	0.00	0.00	36.8	0.00	0.00	0.00
1 hr	0.00	0.00	41.5	0.00	0.00	0.00
	0.00	0.00	43.6	0.00	0.00	0.00
4 hrs	0.00	0.00	39.4	0.00	0.00	0.00
	0.00	0.00	43.8	0.00	0.00	0.00
8 hrs	0.00	0.00	46.0	0.00	0.00	0.00
	0.00	0.00	40.9	0.00	0.00	0.00
24 hrs	0.00	0.00	45.0	0.00	0.00	0.00
	0.00	0.00	45.3	0.00	0.00	0.00
48 hrs	0.00	0.00	42.2	0.00	0.00	0.00
	0.00	0.00	46.8	0.00	0.00	0.00

Table A21. Kinetic study results for Tetryl.

	Concentration (µg/g)					
Time	Soil #1	Soil #2	Soil #3	Soil #4	Soil #5	Soil #6
5 mins	0.00	0.00	284	0.00	0.00	0.00
	0.00	0.00	274	0.00	0.00	0.00
1 hr	0.00	0.00	316	0.00	0.00	0.00
	0.00	0.00	341	0.00	0.00	0.00
4 hrs	0.00	0.00	326	0.00	0.00	0.00
	0.00	0.00	321	0.00	0.00	0.00
8 hrs	0.00	0.00	328	0.00	0.00	0.00
	0.00	0.00	321	0.00	0.00	0.00
24 hrs	0.00	0.00	357	0.00	0.00	0.00
	0.00	0.00	335	0.00	0.00	0.00
48 hrs	0.00	0.00	345	0.00	0.00	0.00
	0.00	0.00	327	0.00	0.00	0.00

Table A22. Recovery of HMX during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X	0.51	0.89	0.65	1.09	0.85
		1.33	0.00	1.03	0.00
X	1.01	1.57	1.20	0.00	1.28
		1.54	1.34	0.00	1.13
2 X	2.02	2.60	2.45	2.27	2.50
		2.12	2.98	3.05	2.09
5 X	5.06	5.97	5.22	5.60	5.31
		5.86	4.82	5.25	5.14
10 X	10.12	10.22	10.45	9.71	10.54
		9.91	10.56	10.27	9.74
20 X	20.24	20.18	19.75	19.59	20.14
		19.87	20.07	20.08	19.29
50 X	50.6	49.4	51.1	48.7	48.8
		51.1	49.2	50.6	48.6
100 X	101.2	98.7	98.4	98.7	96.4
		98.2	99.9	95.1	96.3

Table A23. Recovery of RDX during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X	0.53	0.44	0.00	0.00	0.00
		0.52	0.00	0.00	0.69
X	1.06	0.56	1.14	1.04	0.88
		1.08	1.29	0.00	0.87
2 X	2.12	2.07	2.67	1.81	1.62
		2.39	2.07	2.58	2.31
5 X	5.30	5.08	5.82	5.39	5.63
		5.32	5.38	5.58	4.76
10 X	10.60	10.08	10.98	9.92	9.32
		10.02	10.39	10.51	10.34
20 X	21.20	20.40	20.20	20.44	20.62
		20.62	20.95	20.41	19.16
50 X	53.0	51.3	51.8	50.4	50.8
		51.5	51.5	49.4	50.4
100 X	106.0	103.5	104.2	103.2	101.0
		104.0	105.2	100.5	101.0

Table A24. Recovery of TNB during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X	0.243	0.29	0.00	0.00	0.00
		0.21	0.00	0.00	0.00
X	0.486	0.41	0.42	0.00	0.00
		0.20	0.00	0.00	0.00
2 X	0.972	0.82	1.47	0.99	0.82
		0.57	0.64	1.22	0.46
5 X	2.43	2.20	3.01	2.35	2.15
		2.67	1.50	2.76	2.49
10 X	4.86	4.33	5.16	5.02	4.74
		4.35	4.84	5.35	4.87
20 X	9.72	9.00	9.56	10.14	10.08
		9.14	10.35	8.80	9.42
50 X	24.3	23.93	24.36	24.04	23.25
		24.19	23.99	24.52	23.78
100 X	48.6	48.1	48.0	48.1	46.8
		46.5	47.5	44.7	46.5

Table A25. Recovery of DNB during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X	0.261	0.24	0.45	0.40	0.41
		0.26	0.22	0.26	0.25
X	0.522	0.34	0.64	0.40	0.23
		0.36	0.59	0.30	0.43
2 X	1.04	0.96	1.03	1.03	1.11
		0.96	1.04	0.91	1.11
5 X	2.61	2.76	2.68	2.29	2.52
		2.63	2.64	2.30	2.56
10 X	5.22	5.06	4.94	4.78	4.45
		4.98	5.15	4.92	4.92
20 X	10.44	10.35	9.85	10.11	9.92
		10.18	10.15	10.32	9.73
50 X	26.10	25.59	25.47	25.07	24.83
		25.31	25.21	24.48	24.85
100 X	52.2	50.9	51.0	50.7	49.6
		50.9	51.8	48.9	49.9

Table A26. Recovery of Tetryl during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X*	0.53	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00
X*	1.06	0.26	0.00	0.00	0.00
		0.59	0.00	0.00	0.00
2 X	2.11	1.06	1.81	0.17	0.26
		2.26	2.31	1.95	0.00
5 X	5.28	4.32	2.76	2.39	2.98
		4.38	3.25	2.49	2.60
10 X	10.56	8.87	8.37	6.42	5.61
		8.34	7.36	5.76	5.65
20 X	21.12	15.38	19.13	16.83	16.64
		17.28	18.80	14.81	14.91
50 X	52.8	50.1	51.2	45.9	48.2
		52.6	51.5	48.5	46.7
100 X	105.6	106.5	100.5	104.0	102.6
		105.9	97.3	88.3	97.7

*Data from these levels not used for calculation of detection limits.

Table A27. Recovery of TNT during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X*	0.26	0.00	0.00	0.28	0.00
		0.00	0.00	0.00	0.00
X	0.51	0.21	0.24	0.00	0.00
		0.48	0.00	0.06	0.98
2 X	1.02	1.04	1.16	1.17	1.20
		0.59	1.04	1.47	0.99
5 X	2.55	2.87	3.16	2.91	2.87
		2.94	2.72	3.14	2.93
10 X	5.095	5.56	5.18	5.41	4.68
		5.30	5.52	5.55	4.35
20 X	10.19	11.33	9.90	10.56	9.79
		10.42	10.15	11.74	10.57
50 X	25.48	26.19	25.68	25.66	24.46
		25.13	23.83	25.08	24.69
100 X	50.95	50.4	52.0	50.7	49.1
		52.4	53.2	51.4	50.1

*Data from this level not used to calculate detection limits.

Table A28. Recovery of 2,4-DNT during four-day spike-recovery study.

Spike level	Spiked Concentration (µg/g)	Found Concentration (µg/g)			
		Day 1	Day 2	Day 3	Day 4
0.5 X*	0.039	0.00	0.00	0.00	0.00
		0.00	0.00	0.00	0.00
X*	0.078	0.00	0.00	0.00	0.15
		0.086	0.00	0.00	0.00
2 X	0.156	0.092	0.214	0.00	0.00
		0.198	0.271	0.215	0.00
5 X	0.39	0.24	0.38	0.41	0.40
		0.27	0.39	0.30	0.35
10 X	0.78	0.36	0.81	0.58	0.72
		0.71	0.94	1.02	0.67
20 X	1.56	1.80	1.91	1.61	1.74
		1.50	1.75	1.69	1.52
50 X	3.9	3.82	4.08	3.35	3.54
		3.75	3.64	3.76	3.78
100 X	7.8	7.69	7.68	7.68	7.42
		8.11	7.74	7.39	7.74

*Data from these levels not used to calculate detection limits.

Table A29. Results of filtration experiment for HMX in 50:38:12 water-methanol-acetonitrile

Low Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	253	227	233	235
Millex-HV	223	232	243	211
Nalgene (green)	252	230	249	229
Millex-SR	237	241	227	254
Spartan-T	232	230	228	245
Bio Rad Prep Disc	241	235	219	224
Spartan 3	242	243	232	256
Spartan 25	249	231	220	243
Nalgene (yellow)	228	243	235	248
Spectra/Por	232	236	271	256
Gelman Acro LC25	252	234	237	232
Nuclepore	227	236	237	229

High Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	476	466	473	481
Millex-HV	492	509	478	531
Nalgene (green)	460	478	494	469
Millex-SR	485	481	505	475
Spartan-T	489	500	436	452
Bio Rad Prep Disc	470	467	479	484
Spartan 3	467	476	479	485
Spartan 25	529	461	510	468
Nalgene (yellow)	482	468	474	473
Spectra/Por	474	480	518	494
Gelman Acro LC25	500	459	478	490
Nuclepore	498	526	473	523

Table A30. Results of filtration equipment for RDX in 50:38:12 water-methanol-acetonitrile

Low Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	206	204	199	210
Millex-HV	198	216	206	213
Nalgene (green)	212	208	213	216
Millex-SR	207	202	203	204
Spartan-T	198	207	205	201
Bio Rad Prep Disc	208	215	205	212
Spartan 3	209	205	194	199
Spartan 25	209	201	201	201
Nalgene (yellow)	200	199	221	204
Spectra/Por	201	218	201	209
Gelman Acro LC25	199	211	211	216
Nuclepore	203	209	206	200

High Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	407	395	420	417
Millex-HV	401	410	408	412
Nalgene (green)	403	416	406	397
Millex-SR	392	393	421	393
Spartan-T	393	404	384	387
Bio Rad Prep Disc	394	397	396	388
Spartan 3	396	393	401	421
Spartan 25	394	392	396	411
Nalgene (yellow)	393	412	393	388
Spectra/Por	404	396	405	427
Gelman Acro LC25	413	385	386	400
Nuclepore	385	390	391	400

Table A31. Results of filtration experiment for TNT in 50:38:12 water-methanol-acetonitrile

Low Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	106.7	100.5	104.1	115.2
Millex-HV	110.0	108.7	101.8	108.6
Nalgene (green)	110.6	120.2	100.0	95.5
Millex-SR	101.2	102.8	103.8	112.3
Spartan-T	113.3	106.3	110.4	120.7
Bio Rad Prep Disc	114.7	111.1	116.0	116.1
Spartan 3	110.9	114.2	104.4	107.9
Spartan 25	100.9	106.3	108.0	94.8
Nalgene (yellow)	109.3	97.7	107.9	113.2
Spectra/Por	104.1	112.7	101.7	108.8
Gelman Acro LC25	101.7	108.0	102.2	112.7
Nuclepore	101.0	112.1	106.0	105.8

High Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	219	197	208	209
Millex-HV	199	205	201	200
Nalgene (green)	207	209	212	208
Millex-SR	228	206	205	203
Spartan-T	201	197	194	193
Bio Rad Prep Disc	202	201	216	213
Spartan 3	201	198	212	206
Spartan 25	202	204	212	204
Nalgene (yellow)	204	191	199	200
Spectra/Por	191	212	204	207
Gelman Acro LC25	213	201	203	203
Nuclepore	206	207	202	216

Table A32. Results of filtration experiment for 2,4-DNT in 50:38:12 water-methanol-acetonitrile

Low Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	80.2	73.2	81.0	77.7
Millex-HV	77.6	83.1	72.8	81.3
Nalgene (green)	73.6	82.4	84.3	77.8
Millex-SR	79.7	78.3	80.0	79.2
Spartan-T	91.2	81.5	73.5	81.2
Bio Rad Prep Disc	81.1	77.6	75.9	82.8
Spartan 3	84.7	79.6	74.2	86.7
Spartan 25	73.6	80.8	68.0	77.0
Nalgene (yellow)	70.0	73.2	78.0	77.3
Spectra/Por	75.1	77.2	78.0	76.9
Gelman Acro LC25	77.0	76.4	71.7	79.4
Nuclepore	80.0	77.1	87.2	81.4

High Concentration (µg/L)

Filter type	Replicate 1	Replicate 2	Replicate 3	Replicate 4
Unfiltered	169	148	162	158
Millex-HV	159	153	156	161
Nalgene (green)	152	161	157	165
Millex-SR	166	151	152	159
Spartan-T	170	156	150	154
Bio Rad Prep Disc	163	154	158	156
Spartan 3	155	160	156	161
Spartan 25	151	157	164	152
Nalgene (yellow)	166	153	164	156
Spectra/Por	157	164	165	159
Gelman Acro LC25	171	158	162	156
Nuclepore	147	155	153	159

APPENDIX B. CHEMICAL STRUCTURES

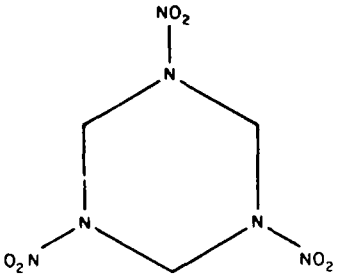

Figure B1. RDX.

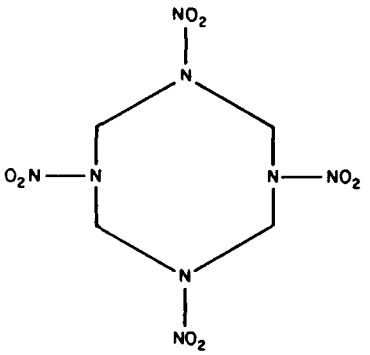

Figure B2. HMX

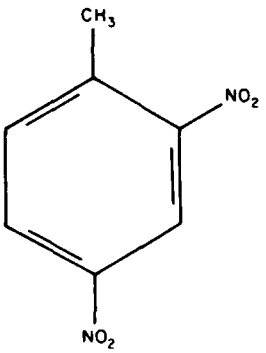

Figure B3. 2,4-DNT.

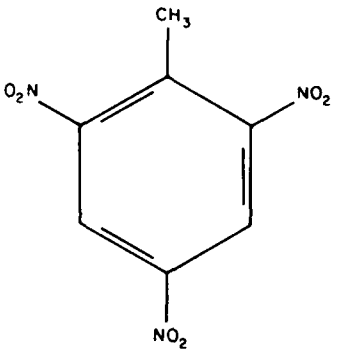

Figure B4. TNT.

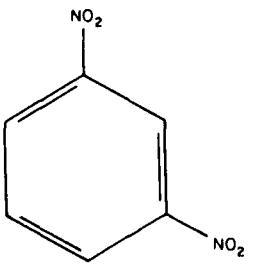

Figure B5. DNB.

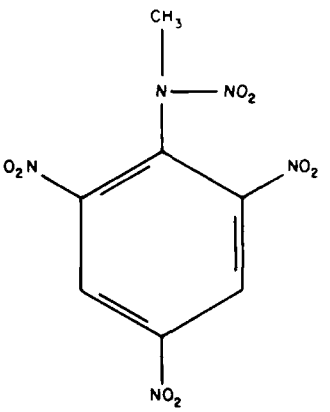

Figure B6. Tetryl.

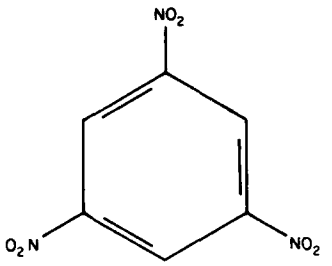

Figure B7. TNB.

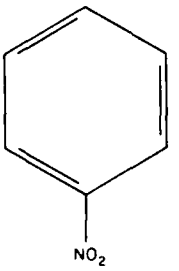

Figure B8. Nitrobenzene.

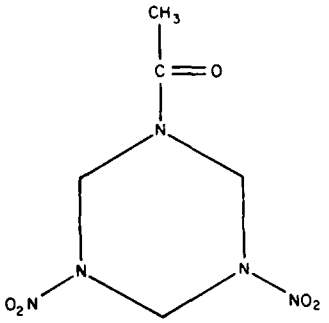

Figure B9. TAX.

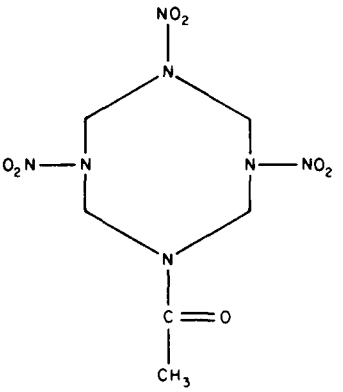

Figure B10. SEX.

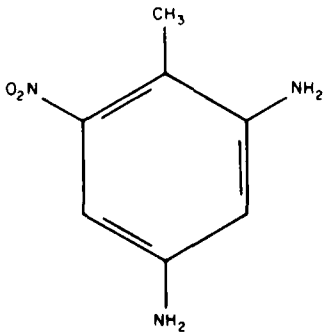

Figure B11. 2,4-DAmNT.

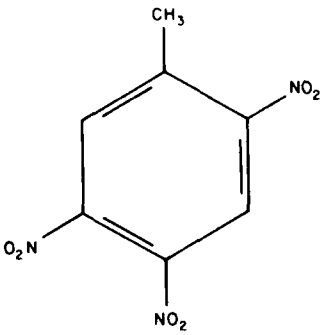

Figure B12. 2,4,5-TNT.

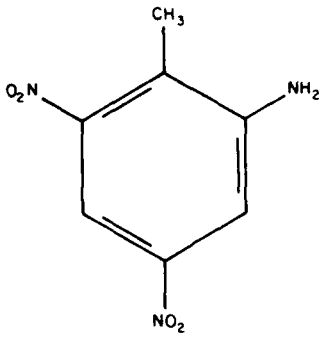

Figure B13. 2-Am-DNT.

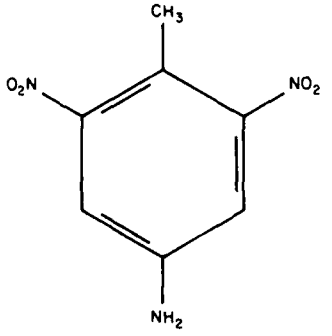

Figure B14. 4-Am-DNT.

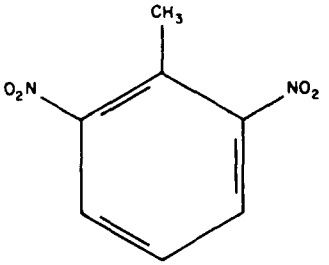

Figure B15. 2,6-DNT.

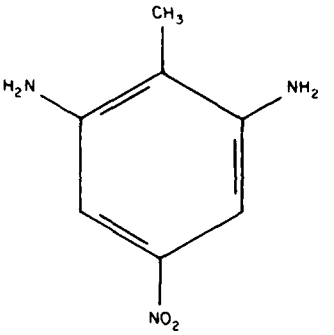

Figure B16. 2,6-DAmNT.

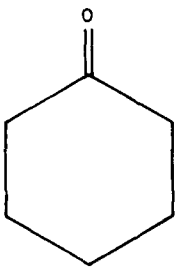

Figure B17. Cyclohexanone.

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Jenkins, Thomas F.
Development of an analytical method for explosive residues in soil / by Thomas F. Jenkins and Marianne E. Walsh. Hanover, N.H.: U.S. Army Cold Regions Research and Engineering Laboratory; Springfield, Va.: available from National Technical Information Service, 1987.
vi, 59 p., illus.; 28 cm. (CRREL Report 87-7.)
Bibliography: p. 19.
1. Analytical methods. 2. Contaminated soils. 3. Explosives. 4. High-performance liquid chromatography. 5. Soils. I. Walsh, Marianne E. I. United States. Army. Corps of Engineers. II. Cold Regions Research and Engineering Laboratory, Hanover, N.H. III. Series: CRREL Report 87-7.

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